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On the Thermodynamics of Non-Electrolyte Solutions and Its Technical Applications

III. Systems with Associated Components

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(Received November 25, 1946)

The influence of continuous association of one component on the free energy of a non-electrolyte solution is derived from a few assumptions. The result is in accord with available data for hydrocarbon-alcohol solutions. Systems of two associating components and the general interpretation of the free energy of non-electrolyte solutions are briefly discussed.

1. INTRODUCTION

THE examination of the thermodynamic properties of non-electrolyte solutions reveals a variety of characteristic types. The interpretation of these types is desirable both for the extension of our basic knowledge and for technical applications such as the design of efficient distillation columns.

Systems of an associating and a non-associating component represent one of these types, easily recognized in a diagram of the function $\log(\gamma/\gamma_0)$ (γ and γ_0 activity coefficients) against the mole fraction x. The advantages of the examination of this particular function and its representation by

$$\log(\gamma/\gamma_0) = B(1-2x)+C[-1+6x(1-x)] + D(1-2x)[1-8x(1-x)]+\cdots, \quad (1)$$

have been discussed in the second paper of this series.[1] It has been found that associating systems can be approximated by (1) with appreciable values of the coefficients B and D, while C is small.

[1] To be published in Ind. and Eng. Chem.

It is the object of this paper to derive this peculiar behavior from a suitably chosen model. In other words, an attempt is made to find the relationship between the free energy and the stoichiometric mole fraction x for a solution which consists of molecules H of a non-associating substance like a hydrocarbon and monomeric and associated molecules A, A_2, $A_3\cdots A_g\cdots$ of an associated substance like an alcohol.

Obviously this problem can be solved only by means of an approximation which is based on far-reaching simplifying assumptions. The decisive point is the proper selection of the assumptions. If they are not far-reaching enough, the calculation becomes too complicated and the number of empirical constants so large that the result has no value at all. On the other hand, the assumptions should not slur over any characteristic feature, and above all, they must be consistent.

The relations derived in this paper are based on three assumptions, each of which is more or less well supported by previous knowledge. They are:

(a) The free energy of interaction can be approximated by Scatchard's method.[1a]

(b) The non-ideal or interaction parts of partial molal quantities (free energy, heat content, volume) of members of a homologous series are proportional to the molecular size. This is a somewhat generalized form of a hypothesis which has been introduced first by Kratky and Musil[2] in a study of the osmotic pressure of high polymers. It has been used since by many authors in this field.

The justification of this assumption lies in the fact that the non-ideal functions directly represent the interaction between molecules, and that any part of a molecule (like an OH-group or a CH_2-group) interacts with its environment approximately the same way irrespective of being part of a larger or a smaller molecule.

(c) It is assumed that the association constant for the reaction

$$A+A_{g-1}=A_g$$

does not depend on the order g of the association. This hypothesis has been considered by Lassettre,[3] later used by Kempter and Mecke[4] and thoroughly discussed by other authors.[5] The basic idea is similar to that of the second assumption.

The three assumptions differ in significance. Assumptions (a) and (b) are fair approximations required for a reasonably simple derivation. Assumption (c), however, restricts the discussion to a certain type of association. Other types undoubtedly exist. For instance, for a solution of acetic acid in a hydrocarbon association to double molecules rather than "continuous" association should be expected.

Starting from different assumptions, Flory[5a] and Tobolsky and Blatz[5b] obtained a different result for a related problem.

[1a] G. Scatchard, Chem. Rev. **8**, 321 (1931); J. Am. Chem. Soc. **56**, 995 (1934); Trans. Faraday Soc. **33**, 160 (1937).
[2] O. Kratky and A. Musil, Oesterr. Chem. Ztg. **40**, 144 (1937); Z. Elektrochemie **43**, 326 (1937).
[3] E. N. Lassettre, J. Am. Chem. Soc. **59**, 1383 (1937); Chem. Rev. **20**, 281 (1937).
[4] H. Kempter and R. Mecke, Zeits. f. physik. Chemie (B) **46**, 229 (1940).
[5] J. N. Wilson, Chem. Rev. **25**, 400 (1939); R. S. Rasmussen, Thesis, California Institute of Technology, Pasadena (1941); J. Kreuzer and R. Mecke, Zeits. f. physik. Chemie (B) **49**, 309 (1941); E. G. Hoffman, *ibid.* **53**, 179 (1943); J. Kreuzer, *ibid.* **53**, 213 (1943).
[5a] P. J. Flory, J. Chem. Phys. **14**, 49 (1946).
[5b] A. V. Tobolsky and P. J. Blatz, J. Chem. Phys. **13**, 379 (1945).

2. NOTATION

The present problem requires a clear distinction between stoichiometric and "true" mole numbers and fractions. The symbol x is used for the stoichiometric mole fraction of the associating substance (alcohol) so that $1-x$ represents the stoichiometric mole fraction of the non-associating component (hydrocabon). The "true" mole numbers, etc., are denoted according to the following scheme:

molecule	H	A	A_2	$A_3 \cdots A_g \cdots$
mole number	n_0	n_1	n_2	$n_3 \cdots n_g \cdots$
mole fraction	N_0	N_1	N_2	$N_3 \cdots N_g \cdots$
activity coefficient	β_0	β_1	β_2	$\beta_3 \cdots \beta_g \cdots$.

We adopt the rule that the symbol $\sum$ indicates summation over the values 1, 2, 3$\cdots$ of the subscript, not including zero.

With

$$n=\sum n_g; \quad N=\sum N_g; \quad N^*=\sum gN_g \tag{2}$$

the relations between the quantities so far introduced are

$$N_0=\frac{n_0}{n_0+n}; \quad N_h=\frac{n_h}{n_0+n}; \quad N=\frac{n}{n_0+n}=1-N_0;$$

$$N^*=\frac{\sum gn_g}{n_0+n}; \tag{3}$$

$$x=\frac{n_1+2n_2+3n_3+\cdots}{n_0+n_1+2n_2+3n_3+\cdots}=\frac{\sum gn_g}{n_0+\sum gn_g}, \tag{4}$$

since a polymerisate of g single alcohol molecules contributes g molecules to the analytical or stoichiometric mole number. The last equation can be transformed, by means of (3), in the following way

$$x=\frac{N^*}{N_0+N^*}; \quad 1-x=\frac{N_0}{N_0+N^*}; \quad \frac{x}{1-x}=\frac{N^*}{1-N}. \tag{5}$$

The significance of the quantity N and numerous related functions has been discussed at very great length by several authors. Various elaborate systems of nomenclature were suggested. It is obvious that a ratio like N^*/N is some measure of the degree of association, and that other functions can be constructed, any of which characterizes the state of association.

3. THE "TRUE" MOLE FRACTION

Since the free energy will be expressed as a function of the "true" mole fraction N, the relationship between this function and the stoichiometric mole fraction x is required. It can be derived from the assumptions (b) and (c).

According to (c), the association equilibrium is characterized by

$$N_g\beta_g = KN_1\beta_1 \cdot N_{g-1}\beta_{g-1}, \tag{6}$$

where K has the same value for all values of g. Repeated application of this equation to the values $g-1$, $g-2\cdots 2$ and multiplication of the obtained relations leads to

$$N_g\beta_g = K^{g-1}(N_1\beta_1)^g. \tag{7}$$

According to assumption (b), the true activity coefficients are connected by

$$\log\beta_g = g\log\beta_1, \tag{8}$$

so that

$$N_g = K^{g-1}N_1^g. \tag{9}$$

Similar formulas have been previously used without justification by assumption (b).

Equations (2) and (9) furnish

$$N = N_1 + KN_1^2 + K^2N_1^3 + \cdots = \sum (KN_1)^g/K = N_1/(1-KN_1); \tag{10}$$

$$N_1 = N/(1+KN);$$

$$dN/dN_1 = 1 + 2KN_1 + 3(KN_1)^2 + \cdots = \sum g(KN_1)^g/KN_1 = 1/(1-KN_1)^2, \tag{11}$$

so that, with the aid of (2) and (9)

$$N^* = \sum gN_g = \sum g(KN_1)^g/K = N_1/(1-KN_1)^2. \tag{12}$$

Equation (10) furnishes

$$(1+KN) = 1/(1-KN_1);$$
$$N(1+KN) = N_1/(1-KN_1)^2. \tag{13}$$

From (5), (12), and (13) we obtain

$$N^* = (1-N)x/(1-x) = N(1+KN) \tag{14}$$

or, arranged in powers of N,

$$N^2 + N/[K(1-x)] - x/[K(1-x)] = 0, \tag{15}$$

so that

$$N = \{-1 + [1+4Kx(1-x)]^{\frac{1}{2}}\}/[2K(1-x)]. \tag{16}$$

The negative sign of the root is excluded by the fact that N must be positive. This formula satisfies, of course, the obvious conditions

$$N = x \text{ for } K = 0; \tag{17}$$

$$N = 0 \text{ for } x = 0; \tag{18}$$

$$N = 1 \text{ for } x = 1. \tag{19}$$

The application of this relation will be discussed later.

4. THE FREE ENERGY

The free energy will be represented in two ways. First, in the conventional way by means of the stoichiometric and experimental quantities:

$$(F-F^0)/2.3RT = (1-x)\log(1-x) + x\log x + Q, \tag{20}$$

where the function

$$Q = (1-x)\log\gamma_0 + x\log\gamma \tag{21}$$

corresponds to Scatchard's "excess free energy." The activity coefficients of the hydrocarbon and the alcohol are denoted by γ_0 and γ, respectively. The quantities F and Q refer to that amount of solution which contains $(1-x)$ moles of hydrocarbon and x moles of alcohol.

The free energy can also be represented in terms of the "true" mole fractions:

$$(F-F^0)/2.3RT = (N_0\log N_0 + \sum N_g\log N_g + Q^*)/(N_0+N^*), \tag{22}$$

$$Q^* = N_0\log\beta_0 + \sum N_g\log\beta_g, \tag{23}$$

where the "true" activity coefficients are denoted by β_0 and β_g. The denominator N_0+N^* reduces the right hand side of (22) to the amount of solution containing $1-x$ and x moles of the components since the numerator refers to N_0 moles of hydrocarbon and $\sum gN_g = N^*$ moles of monomeric alcohol.

According to assumption (a) the quantity Q^* can be represented by Scatchard's equation

$$Q^* = (\sum b_{0g}V_0V_gN_0N_g + \sum b_{gh}V_gV_hN_gN_h)/(V_0N_0 + \sum V_gN_g), \tag{24}$$

where b_{0g} denotes Scatchard's coefficient of interaction between a solvent molecule and a polymer of order g, divided by $2.3RT$. The coefficient b_{gh} indicates the interaction of two polymers of order g and h. Since Q^* is a homogeneous function of first degree in N_0 and N_g, the activity coef-

ficients are given by

$$\log\beta_0=\partial Q^*/\partial N_0;\quad \log\beta_g=\partial Q^*/\partial N_g. \quad (25)$$

It can be concluded from Tyrer's measurements[6] of the densities of methanol-benzene solutions that the apparent molal volume of the alcohol varies not more than a few tenths of one percent over the whole range. The approximation

$$V_g=gV_1 \quad (26)$$

is therefore amply sufficient. By introducing (26) into (24) and carrying out the differentiation indicated in (25), one recognizes that condition (8) requires that the interaction coefficients b_{0g} and b_{gh} be independent of the subscripts g and h, i.e., that

$$b_{0g}=b_{01};\quad b_{gh}=b_{11}, \quad (27)$$

whatever the values of g and h are.

Equations (24) to (27) furnish

$$\begin{aligned}\log\beta_0&=V_0(b_{01}-b_{11})z^2;\\ \log\beta_g&=gV_1[(b_{01}-b_{11})(1-z^2)+b_{11}],\end{aligned} \quad (28)$$

where

$$\begin{aligned}z&=V_1N^*/(V_0N_0+V_1N^*)\\ &=V_1x/[V_0(1-x)+V_1x]\end{aligned} \quad (29)$$

represents the volume fraction of the alcohol.

The change from the "true" to the experimental or stoichiometric activity coefficients can be carried out by means of (20) to (23). More convenient is a direct calculation based on the fact that the activities, as experimental quantities, do not depend on any assumption regarding the molecular state. Denoting the activities in the reference states by a_0^0 and a_1^0, we have, therefore,

$$(1-x)\gamma_0=N_0\beta_0/a_0^0;\quad x\gamma=N_1\beta_1/a_1^0. \quad (30)$$

From (3), (5), (10), and (14), we derive

$$\begin{aligned}N_0/(1-x)&=N_0+N^*=1-N+N^*\\ &=1+KN^2;\end{aligned} \quad (31)$$

$$\frac{N_1}{x}=\frac{N}{1+KN}\cdot\frac{N_0+N^*}{N^*}=\frac{1+KN^2}{(1+KN)^2}. \quad (32)$$

Equations (28) to (32) furnish

$$\begin{aligned}\log\gamma_0&=\log(1+KN^2)\\ &\quad+V_0(b_{01}-b_{11})z^2+\log a_0^0;\end{aligned} \quad (33)$$

$$\begin{aligned}\log\gamma&=\log[(1+KN^2)/(1+KN)^2]\\ &\quad+V_1[(b_{01}-b_{11})(1-z)^2+b_{11}]+\log a_1^0.\end{aligned} \quad (34)$$

The reference states are defined by the usual convention that

$$\log\gamma_0=0 \text{ for } x=0;\quad \log\gamma=0 \text{ for } x=1, \quad (35)$$

the corresponding limits $N=0$ and $N=1$ being given by (18) and (19). Therefore,

$$\begin{aligned}\log\gamma&=\log[(1+K)(1+KN^2)/(1+KN)^2]\\ &\quad+V_1(b_{01}-b_{11})(1-z)^2.\end{aligned} \quad (36)$$

The function $\log(\gamma/\gamma_0)$ is useful for a comparison with experimental data. With the abbreviation

$$A=2x\log(1+K)-2\log(1+KN) \quad (37)$$

it is represented by

$$\begin{aligned}\log(\gamma/\gamma_0)&=A+(1-2x)\log(1+K)\\ &\quad+(b_{01}-b_{11})[V_1(1-z)^2-V_0z^2].\end{aligned} \quad (38)$$

Developing the expression in brackets in terms of

$$v=(V_1-V_0)/(V_1+V_0), \quad (39)$$

one obtains

$$\begin{aligned}V_1(1-z)^2-V_0z^2&=2V_1V_0/(V_1+V_0)\\ &\quad\times\{1-2x-v[-1+6x(1-x)]+\cdots\}.\end{aligned} \quad (40)$$

The term containing v is a second order term which is outside the scope of the present discussion. Indeed, the error introduced by (27) can be estimated in a somewhat complicated calculation and is found to be of the same order of

TABLE I. Values of the association function A. (− sign for $0<x<\frac{1}{2}$; + sign for $\frac{1}{2}<x<1$.)

K	x / x	0.05 / 0.95	0.1 / 0.9	0.2 / 0.8	0.3 / 0.7	0.4 / 0.6
1		0.0107	0.0163	0.0199	0.0165	0.0090
2		.0290	.0433	.0494	.0396	.0224
3		.0486	.0702	.0777	.0610	.0330
4		.0680	.0962	.1036	.0801	.0429
5		.0870	.1206	.1269	.0976	.0519
6		.1049	.1426	.1475	.1126	.0600
8		.1386	.1835	.1854	.1397	.0738
10		.1693	.2193	.2176	.1625	.0856
12		.1974	.2512	.2457	.1825	.0959
14		.2233	.2800	.2707	.2001	.1049
16		.2472	.3063	.2933	.2160	.1130
20		.2904	.3528	.3328	.2434	.1268
25		.3376	.4024	.3742	.2722	.1416
30		.3786	.4450	.4094	.2966	.1512

[6] D. Tyrer, J. Chem. Soc. 99, 871 (1911).

magnitude as the v-term in (40). This term, therefore, will be neglected or taken care of by means of an empirical coefficient so that with

$$B=\log(1+K)+(b_{01}-b_{11})\cdot 2V_1V_0/(V_1+V_0) \quad (41)$$

the result

$$\log(\gamma/\gamma_0)=A+B(1-2x) \quad (42)$$

is obtained.

The linear B-term represents the usual first approximation of the interaction between the two components. The coefficient B, however, contains $\log(1+K)$ and is to be expected, therefore, to be unusually large for associating systems. The "association function" A depends on the association constant K and the mole fraction x in a complicated way and determines the peculiar behavior of systems with an associating component.

5. THE ASSOCIATION FUNCTION

The association function (37) is odd with respect to the variable $(1-2x)$. In other words, if A' represents the value of A for x', and A'' the value for $x''=1-x'$, then $A'+A''=0$. To prove this, we calculate first

$$1+KN=(1-2x+r)/2(1-x); \qquad r=+[1+4Kx(1-x)]^{\frac{1}{2}} \quad (43)$$

from (16). Then we see that, since $r'=r''$,

$$(1+KN')(1+KN'')=(1-2x+r)\times(-1+2x+r)/4x(1-x)=1+K, \quad (44)$$

after an appropriate rearrangement. Equation (37) then furnishes

$$A'+A''=2(x+1-x)\log(1+K)-2\log(1+K)=0. \quad (45)$$

For small values of K, the square root r can be developed into a power series. The development up to the second order furnishes

$$A=K^2x(1-x)(2x-1)/2.303, \quad (46)$$

valid for small values of K and any value of x.

Likewise one obtains for small values of x and any value of K

$$A=2x[\log(1+K)-K/2.303]. \quad (47)$$

If $K\ll 1$ and therefore (46) holds, Eq. (42) is represented by (1) with

$$C=0; \quad -8D=K^2/2.303, \quad (48)$$

i.e., the association function furnishes the D-term. For greater values of K appreciable deviations arise though the general course is still similar. It has been realized already by Scatchard that association leads to a term of this type.

Table I contains values of the function A.

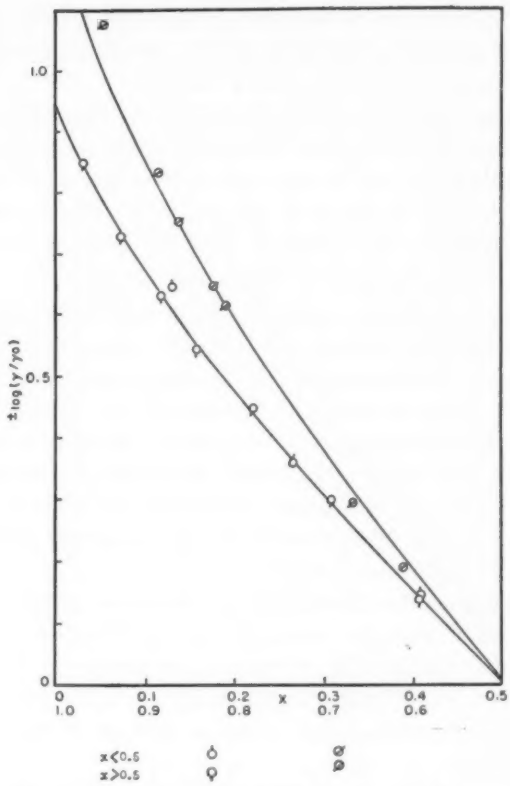

FIG. 1. Toluene-methanol and n-heptane-methanol (760 mm).

6. EXPERIMENTAL DATA

The results of Benedict[7] *et al.* on toluene-methanol and n-heptane-methanol at atmospheric pressure are shown in Fig. 1. In this figure, the absolute magnitudes of the function (42) are plotted against the mole fraction x of the associating component in such a way, that the values x and $(1-x)$ of the abscissa coincide. In a diagram of this kind, the two branches of $[\log(\gamma/\gamma_0)]$ are represented by a single curve if, and only if, log

[7] M. Benedict, C. A. Johnson, E. Solomon, and L. C. Rubin, Trans. Am. Inst. Chem. Eng. **41**, 371 (1945).

(γ/γ_0) is an odd function of $(1-2x)$, i.e., if the values of $\log(\gamma/\gamma_0)$ for x and $(1-x)$ have opposite sign and equal magnitude.

The data of Benedict *et al.* were checked by means of the method described in the first paper of this series and found very well consistent. The scattering, as shown in Fig. 1, is small. The diagram shows immediately that the two branches of $[\log(\gamma/\gamma_0)]$ for $x<0.5$ and $x>0.5$ can be represented by a single curve which deviates considerably from a straight line. The curve for toluene-methanol in Fig. 1 corresponds to Eq. (42) with $B=0.95$ and $K=3.8$ in the association function (37). This curve represents the data well within the small experimental errors. The data for *n*-heptane-methanol are fairly well represented by the curve in Fig. 1 corresponding to $B=1.25$ and $K=6.6$

The results of Ferguson[8] on *n*-hexane-methanol at 45°C can be represented by $B=1.71$ and $K=30$. Data for *n*-heptane-ethanol[9] at 30°C scatter considerably more. Even so, the expected influence of the association of ethanol is unmistakable.

In these examples the coefficient C (Eq. (1)) is practically zero. Frequently, however, an additional, usually small, C-term is required for the representation of experimental data. Recently published data[10] of benzene-methanol for 35°C are satisfactorily represented by means of $B=1.050$; $C=-0.116$; $K=6.1$, the data on carbon tetrachloride-methanol by means of $B=1.105$; $C=-0.148$; $K=6.1$. The deviations of the mole fraction of the vapor and of the pressure are of the same order as those obtained by Scatchard, Wood and Mochel with three independent coefficients for each system.

The characteristic influence of association is more or less clearly noticeable in the data available for benzene-phenol,[11] benzene-aniline and benzene-benzonitrile,[12] benzene-propanol,[13] and in various systems with ethanol and butanol.[14]

The association indicated by the vapor pressures of the system triethylamine-water[15] is undoubtedly due to water since triethylamine is not appreciably associated.[16]

A qualitative check may be seen in the fact that the values of B are very large and that the values of K, with the exception of $K=30$ for hexane-methanol, are reasonable. No term similar to the association function A has been found in any system of non-associating components. It may be concluded, therefore, that this function actually is characteristic of associating systems.

According to (10) and (19), the mole fraction of the monomer in the pure alcohol is

$$N_1=1/(1+K). \qquad (49)$$

Since this quantity as a property of the pure component cannot depend on the nature of the other component, the present model requires that the association constant be a property of the alcohol.

Since K is extremely sensitive against experimental errors, only very accurate data can contribute to a test of this conclusion. The data of Benedict *et al.*[7] were obtained at atmospheric pressure, i.e., at varying temperatures. However, most of the measurements on toluene-methanol ($K=3.8$) were carried out in the neighborhood of 64°, those on heptane-methanol ($K=6.6$) close to 58°.

The association constants for methanol derived at 64° (with toluene) and 35° (with benzene and carbon tetrachloride) lead to the reasonable value of 3300 cal./mole for the heat of association. The value $K=4.4$ resulting for 55° has been used to represent the data obtained by Scatchard, Wood and Mochel[10] at this temperature for the systems with benzene ($B=0.981$; $C=-0.113$) and carbon tetrachloride ($B=1.027$; $C=-0.120$). Here, too, the deviations of the mole fraction of the vapor and of the pressure are of the same order as in the equations of Scatchard *et al.* with three independent coefficients.

The interpolation between 35 and 64° leads to $K=5.1$ at 45° and $K=4.2$ at 58°. The deviations of the values 30 (with hexane) and 6.6 (with

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[16] R. T. Lattey, J. Am. Chem. Soc. **91**, 1959 (1907).

heptane) derived directly from experimental data for these two temperatures are probably due to errors in the measurements.

The best test of the present results would be a comparison of the association constants derived from vapor pressures with values obtained from the intensity of infra-red absorption bands of the hydroxyl group. At present no data are available for this comparison. Further tests could be made in connection with data on dielectric constants (cf. Wilson[5]), the frequencies of the hydroxyl bands (cf. Rasmussen[5]) and with data on heats of mixing.

7. SYSTEMS OF TWO ASSOCIATING COMPOUNDS

If both components associate, one has, in the general case, to consider bonds between molecules of the first component (equilibrium constant K'), between molecules of the second component (K''), from a molecule of the first kind to one of the second (K''') and conversely (K^{iv}). Even with the far-reaching assumptions introduced in the first section, the general case leads to difficulties of such extent that a thorough treatment does not appear to be worth while. But quantitative results can be easily derived for two special cases. They are limiting cases of such nature that the whole field appears to be qualitatively covered.

If the association constants for all four types of bonds are equal, $K'=K''=K'''=K^{iv}$, no association term at all appears in the free energy. This somewhat surprising result seems to be in satisfactory agreement with data for systems both components of which tend equally to the formation of hydrogen bonds like systems of two alcohols.

The second special case is characterized by the absence of interassociation between the components, $K'''=K^{iv}=0$. One will expect that this case is realized only by a kind of association entirely different from that caused by hydrogen bonds. A calculation which runs strictly parallel to the course followed in the third and fourth section of this paper furnishes again Eqs. (37) and (42) with

$$K=K'+K''+K'K''. \tag{50}$$

In other words, a system of this kind behaves just like a system with a single associating component, except that the "apparent" association constant has a different significance.

The system benzene-cyclohexane appears to be an example of this kind. Scatchard, Wood and Mochel[17] have already interpreted their measurements by means of association. The association is so small in this case that the influence of the volumes as indicated by (38) is still significant. The approximation (46) is valid. The experimental data are satisfactorily represented by (38) with $b_{01}-b_{11}=0.001133$; $K=0.244$ (40°C) and $b_{01}-b_{11}=0.000796$; $K=0.184$ (70°C).

The results obtained so far indicate a fairly simple general interpretation of the thermodynamic properties on non-electrolyte solutions. The B-term in series (1) is known to represent interaction and the C-term indicates in the simplest cases the influence of the difference of the molal volumes. The D-term indicates the influence of association and is better replaced by the association function A. This interpretation may offer a suitable starting point for a discussion of the coefficients of series (1) in relation with the nature of the components.

The authors wish to express their thanks to Dr. R. W. Millar, Dr. R. S. Rasmussen and Dr. J. N. Wilson for valuable discussions and advice.

[17] G. Scatchard, S. E. Wood, and J. M. Mochel, J. Phys. Chem. **43**, 119 (1939).

THE JOURNAL OF CHEMICAL PHYSICS VOLUME 15, NUMBER 12 DECEMBER, 1947

Foreign Ion Rejection in the Growth of Sodium Chloride Single Crystals from the Melt*

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(Received June 20, 1947)

A study is made of the process of purification that takes place when single crystals are grown from the melt. The rejection of potassium and copper ions from solid solution in sodium chloride crystals is measured quantitatively by analyzing by spectrochemical means sections of cylindrical crystals of sodium chloride to which has been added a known quantity of impurity. The theory of the distribution of impurity over the height of the crystal is derived in terms of the initial impurity concentration, height of completed crystal, and the fraction of the impurity concentration in the melt included in the crystal, which fraction is called the purification coefficient. Good agreement is obtained between theory and experiment for an initial concentration of 0.1 atomic percent potassium in sodium chloride. Purification coefficients for several crystals containing potassium and a few crystals containing copper are measured and correlated with rate of growth and temperature gradient conditions.

INTRODUCTION

A GOOD single crystal which is to be used for optical purposes is characterized by its lack of excessive absorption of radiation in the optical spectrum. The increased absorption which is exhibited by inferior optical crystals is due, in general, to the presence of distributed impurities,*** which may consist of ions of a foreign material in solid solution or of neutral atoms of one of the ionic constituents. The growth conditions for an optical crystal are usually adjusted experimentally to give maximum rejection of these impurities. Stockbarger[1] found that in order to produce optical lithium fluoride crystals extremely pure raw material must be used, and the crystallizing conditions adjusted very carefully. It was observed that additional impurity material appeared at the top of the crystal after growth from the bottom upward. The phenomenon of the purification of materials by recrystallization from the melt has been utilized before. Davey[2] mentions that certain crystalline materials have been purified by fusing and allowing to recrystallize slowly.

In order to make some quantitative measurements of the rejection of foreign ions in solid solution in the process of the growth of an ionic crystal a representative crystal was selected which would lend itself to the method of study. Sodium chloride was chosen because of the ease in growing single crystals from C.P. grade material, and its water solubility, which would facilitate the analysis of the crystals. Two foreign ions were selected as impurities: potassium and bivalent copper, both in the form of the chloride. The selection of impurity ions was also restricted by consideration of the analytical problem, which in this case involved the spectrochemical method.

EXPERIMENTAL METHOD

Growth of Crystals

The general method of Bridgman,[3] as modified by Stockbarger,[1,4] was used to grow the single crystals. Twenty-five grams of C.P. sodium chloride, to which was added an impurity chloride in the proportion 0.1 atomic percent impurity to sodium, was crystallized in a conical bottom platinum crucible 19 mm in diameter and 75 mm long. The completed crystal was 19 mm in diameter and 44 mm long. Crystallization was accomplished by melting the powdered stock in a region of the furnace kept at a temperature above the melting point, then lowering the

* Taken from a thesis submitted in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Physics from the Massachusetts Institute of Technology, 1943.

** Now with Photoswitch Incorporated, Cambridge, Massachusetts.

*** Absorption caused by "*F*" centers is not ordinarily observed in freshly prepared synthetic crystals.

[1] D. C. Stockbarger, Rev. Sci. Inst. **7**, 133 (1936).

[2] W. P. Davey, *Crystal Structure and its Applications* (McGraw-Hill Book Company, Inc., New York, 1934).

[3] P. W. Bridgman, Proc. Am. Acad. **60**, 305 (1925).

[4] D. C. Stockbarger, J. Opt. Soc. Am. **27**, 416 (1937).

crucible containing the melt slowly through an annular baffle into a region of the furnace which was below the melting point, causing the crystal to grow upward from the pointed bottom. Temperatures were adjusted so that crystallization took place close to the level of the baffle. The crystallizing arrangement is shown Fig. 1.

The temperature gradient existing in the melt near the crystallizing level was measured by means of a platinum-platinum, 10 percent rhodium thermocouple situated at a fixed position inside the crucible (Fig. 1, *E*). Temperature readings were taken at intervals, as the thermocouple and crucible were lowered at a constant rate, until just before crystallization took place at the level of the thermocouple junction, when the thermocouple was extracted. The temperature was found to decrease uniformly from about 50°C above the crystallizing point, then to decrease uniformly at a slightly greater rate in the crystal. The effective temperature gradient was taken as the quotient of the slope of the temperature *vs.* time plot in the melt near the crystallizing point and the rate of growth.

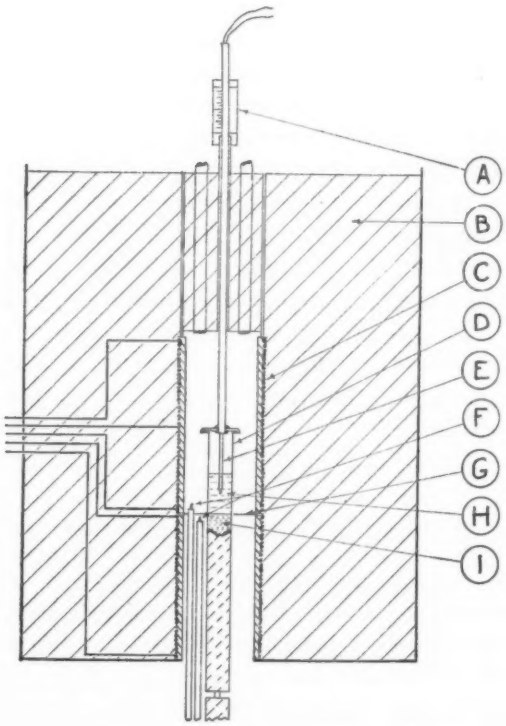

FIG. 1. Crystal growing furnace: *A* = thermocouple depth gauge; *B* = fire brick insulation; *C* = alundum furnace core with No. 16 Nichrome heater winding; *D* = platinum crucible; *E* = gradient thermocouple; *F* = furnace thermocouples; *G* = baffle; *H* = melt; *I* = crystal.

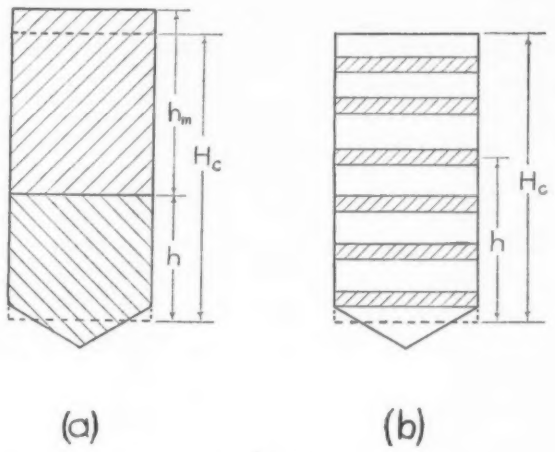

FIG. 2.

The rate of growth was determined by the rate at which the crucible assembly was lowered by the elevator mechanism. This mechanism consisted of an adjustable gear train driven by a small synchronous motor and connected to a rack on the elevator shaft.

The level of crystallization was determined by means of a platinum wire probe which dipped into the melt through the top. With the furnace arrangement shown in Fig. 1 it was found that the position of the crystallizing level relative to the baffle did not change appreciably during the growth of the crystal when the furnace temperatures were properly adjusted.

The furnace temperature was controlled by means of a special temperature regulator[5] operating from the output of the thermocouple projecting into the upper section of the furnace. The temperature at this point was maintained constant within 0.1°C.

The crucible containing the completed crystal was taken out of the furnace, inverted, and the crystal melted out by lowering into the hot furnace again, after the technique of Stockbarger.[3]

Analysis of Crystals

The cylindrical single crystals were placed in a jig which held the crystal while it was sliced perpendicular to the cylinder axis. Two mm thick slices were extracted at separations of

[5] D. C. Stockbarger, Rev. Sci. Inst. **10**, 205 (1939).

TABLE I.

Crystal No.	h/H_e	Rate of growth	Temp. grad.	a_h	a_h/C_0	A	$\bar{A}$	$\bar{A}_R$
56	0.073	1.172	—	0.0174	0.167	0.155	0.157	0.178
	0.229			0.0203	0.195	0.150		
	0.378			0.0256	0.246	0.165		
	0.530			0.0310	0.298	0.158		
	0.694			0.0449	0.431	0.156		
	0.850			0.0800	0.769	0.156		
68	0.378	1.172	3.83	0.0276	0.265	0.181	0.193	
	0.530			0.0387	0.372	0.205		
69	0.378	1.172	7.32	0.0252	0.242	0.165	0.179	
	0.530			0.0365	0.351	0.192		
55	0.229	2.344	—	0.0210	0.202	0.160	0.155	0.175
	0.378			0.0232	0.223	0.151		
	0.530			0.0303	0.291	0.156		
	0.694			0.0415	0.399	0.146		
	0.850			0.0830	0.798	0.164		
57	0.073	2.344	—	0.0192	0.185	0.175	0.163	
	0.229			0.0212	0.204	0.162		
	0.378			0.0261	0.251	0.172		
	0.530			0.0341	0.328	0.178		
	0.694			0.0460	0.442	0.165		
	0.850			0.0670	0.644	0.123		
70	0.378	2.344	4.65	0.0313	0.301	0.209	0.208	
	0.530			0.0388	0.373	0.206		
54	0.073	4.688	—	0.0203	0.195	0.185	0.173	0.196
	0.229			0.0226	0.217	0.171		
	0.378			0.0260	0.250	0.170		
	0.530			0.0331	0.318	0.173		
	0.694			0.0489	0.470	0.179		
	0.850			0.0820	0.788	0.161		
58	0.073	4.688	—	0.0277	0.266	0.251	0.206	
	0.229			0.0245	0.236	0.189		
	0.378			0.0300	0.288	0.198		
	0.530			0.0440	0.423	0.240		
	0.694			0.0520	0.500	0.194		
	0.850			0.0820	0.788	0.161		
59	0.073	4.688	—	0.0200	0.192	0.177	0.186	
	0.229			0.0230	0.221	0.174		
	0.378			0.0302	0.290	0.198		
	0.530			0.0376	0.361	0.195		
	0.694			0.0519	0.499	0.194		
	0.850			0.0880	0.845	0.180		
60	0.378	4.688	—	0.0310	0.298	0.205	0.205	
61	0.378	4.688	—	0.0280	0.269	0.185	0.185	
62	0.378	4.688	—	0.0320	0.308	0.212	0.212	
65	0.378	4.688	7.68	0.0301	0.289	0.200	0.210	
	0.530			0.0410	0.396	0.220		
66	0.378	4.688	3.26	0.0266	0.256	0.174	0.192	
	0.530			0.0393	0.202	0.210		
64	0.378	9.375	2.56	0.0336	0.323	0.224	0.229	0.257
	0.530			0.0440	0.423	0.240		
67	0.378	9.375	7.20	0.0288	0.276	0.190	0.215	
	0.530			0.0440	0.423	0.240		
72	0.378	9.375	7.72	0.0409	0.392	0.278	0.297	
	0.530			0.0550	0.529	0.315		
73	0.378	9.375	6.58	0.0360	0.346	0.242	0.268	
	0.530			0.0520	0.500	0.294		
81	0.530	9.375	4.14	0.0498	0.479	0.278	0.278	
78	0.378	18.75	1.42	0.0509	0.489	0.360	0.360	0.375
82	0.530	18.75	7.23	0.0578	0.555	0.337	0.337	
84	0.530	18.75	3.05	0.0678	0.650	0.423	0.423	
85	0.530	18.75	5.03	0.0667	0.641	0.411	0.411	
86	0.530	18.75	4.64	0.0593	0.570	0.344	0.344	
87	0.530	25.00	5.37	0.0920	0.885	0.715	0.715	0.715

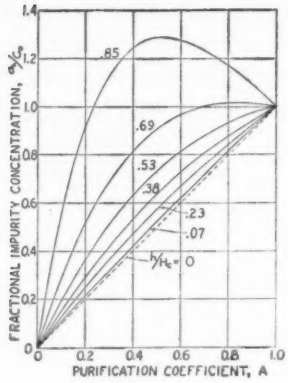

FIG. 3.

about six mm. The concentration of impurity in a slice was taken to represent the concentration at the average height of the slice in the crystal.

Spectrochemical means were used to determine the impurity concentration in the crystal slices. The concentrations were in such a range as to be favorable to this type of microanalysis.

Analyses for potassium in the sodium chloride crystals were made by photographing the spectrum of the material excited by a d.c. arc through a logarithmic step-sector disk. Rubidium chloride was added to the salt as an internal standard for the analysis. Microphotometer measurements of sensitive lines of potassium at λ7665A and rubidium at λ7800A recorded on infrared sensitive film were used as indications of the concentrations.[6]

Concentrations of copper ions were measured by exciting the samples by means of an a.c. high voltage arc. Silver was used as the internal standard in this case. The copper line at λ3274A and the silver line at λ3281A were used for the analyses.

THEORY

Distribution of Impurity Ions in the Crystal

Crystallizing conditions in the above described apparatus are such that the following assumptions may be made, particularly for the single crystals grown at low rates: (1) the rate of growth and temperature gradient remain constant throughout the growth; (2) the impurity ions are distributed uniformly throughout the melt; (3) the foreign ions are contained in solid

[6] L. W. Strock, J. Opt. Soc. Am. **32**, 103 (1942).

solution in the crystal; (4) the phase boundary between melt and crystal is a plane perpendicular to the cylinder axis. Figure 2a represents the picture of the crystal growth. The height dimension is measured from a level one third the altitude of the conical bottom section below the shoulder, corresponding to the bottom of a cylindrical section of equivalent volume.

With constant crystallizing conditions, the probability that an impurity ion will become trapped in the crystal lattice is constant. If the concentration of impurity ions in the melt is small, the fraction of the number of impurity ions per unit mass in the melt that is included in the crystal is a constant. Then the concentration of impurity ions in the crystal, a_h, at a height h is proportional to the concentration of impurity ions in the melt, b_h, at the point when the crystal has grown to a height h, or

$$a_h = Ab_h, \tag{1}$$

where A, the constant of proportionality, may be called the purification coefficient. This quantity never exceeds unity.

From this relation the distribution of impurity ions in a crystal grown under the above crystallizing conditions may be derived. Let dN_m be the change in the total number of impurity ions in the melt when the crystal grows from a height h to a height $h+dh$. The number of impurity ions per unit height in the crystal at height h is then $-dN_m/dh$. If a_h and b_h are expressed in atomic percent impurity ions to sodium ions,

$$a_h = \frac{100}{n_c}\left(-\frac{dN_m}{dh}\right), \tag{2}$$

$$b_h = \frac{100}{n_m}\left(\frac{N_m}{h_m}\right), \tag{3}$$

where n_c is the number of sodium ions per unit height in the crystal, n_m is the number of sodium ions per unit height in the melt, N_m is the total number of impurity ions in the melt, and h_m is the height of the melt.

h_m bears the relation to H_c, the height of the completed crystal,

$$h_m = \frac{n_c}{n_m}(H_c - h). \tag{4}$$

TABLE II.

Crystal No.	h/H_c	Rate of growth	Temp. grad.	a_h	a_h/C_0	A	$\bar{A}$
94	0.530	4.688	1.71	0.0315	0.315	0.170	0.170
75	0.073	4.688	6.40	0.0107	0.107	0.095	0.0644
	0.229			0.0094	0.094	0.070	
	0.378			0.0100	0.100	0.062	
	0.530			0.0145	0.145	0.069	
	0.694			0.0191	0.191	0.061	
	0.850			0.0365	0.365	0.060	
93	0.530	9.375	2.61	0.0518	0.518	0.307	0.307
91	0.530	9.375	6.70	0.0305	0.305	0.163	0.163

By substitution and integration

$$a_h = \frac{100}{n_c}\frac{NA}{H_c}\left[1-\frac{h}{H_c}\right]^{A-1}, \tag{5}$$

where N is the total number of impurity ions present, or

$$a_h/C_0 = A\left[1-\frac{h}{H_c}\right]^{A-1}, \tag{6}$$

where C_0 is the concentration of impurity ions initially present in atomic percent impurity to sodium ions.

Figure 3 shows a plot of the fractional impurity concentration, a_h/C_0, as a function of A for a series of values of h/H_c corresponding to those values for the six sample slices analyzed (Fig. 2b). If a cross section of these curves is taken at a given value of A, the resulting curve represents the relative distribution of impurities throughout the height of a crystal grown under conditions such that the purification coefficient is A.

EXPERIMENTAL RESULTS

The results of measurements taken on twenty-five sodium chloride crystals containing initially

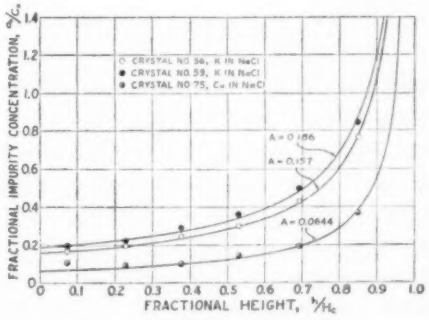

FIG. 4.

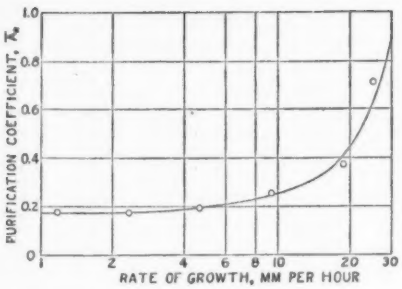

FIG. 5.

0.104 atomic percent potassium (0.100 atomic percent added plus 0.004 atomic percent potassium impurity) are given in Table I. Each crystal used for analysis was homogeneous, single, clear, and colorless. Each measurement of the potassium concentration, a_h, represents the average of five spectrographic determinations. Temperature gradient measurements were taken on crystals from No. 64 on. A values corresponding to the a_h figures were obtained by interpolation in Fig. 3 on the curve representing the level of the sample analyzed. a_h/C_0 represents the fractional impurity concentration, that is, the fraction of the original impurity concentration remaining in the crystal at height h. $\bar{A}$ is the average value of A for the various samples from a single crystal. Since no systematic variation of A with temperature gradient is evident, the average A for all crystals grown at the same rate, $\bar{A}_R$, is taken.

By way of comparison with the results obtained with potassium impurity four crystals containing initially 0.1 atomic percent copper were grown and analyzed (Table II). Crystal number 75 was analyzed over the complete height.

The fractional impurity concentration as related to the height in two crystals containing potassium and in one crystal containing copper are shown in Fig. 4. The points are taken from the experimental data as given in Tables I and II. The solid curves are plotted from the equation for a_h/C_0 (Eq. 6), where A is taken as the average, $\bar{A}$, of the A values of all six samples.

The variation of the average purification coefficient, $\bar{A}_R$, with rate of growth for the potassium-containing crystals, is shown in Fig. 5. Since the point at 25 mm per hour represents only one crystal, its position is not as well established as those of the other points.

DISCUSSION

It would appear from the agreement of the experimental points for the two potassium crystals with the theoretical curves in Fig. 4 that growth conditions approached the ideal ones as postulated in the theory in those instances. The rising tendency for the points at the lower end of the curve taken for the copper-containing crystal may be due to a slight settling out of the heavier copper ions in the melt. As might be expected, the copper impurity is rejected more completely from the crystal than in the potassium, since the latter possesses ionic characteristics more similar to those of sodium. Even in the case of potassium impurity the foreign ion concentration is less than that of the raw material up to a thin layer at the top of the crystal.

Figure 5 and Table I indicate the relation between the degree of purification and the crystallization conditions. Figure 4 is significant in that it shows that a minimum value of potassium concentration is reached at a finite rate of growth, in this case near four millimeters per hour. The apparent random function of the temperature gradient in eliminating potassium from sodium chloride may be due to the insufficiently extensive range of temperature gradients used. However, in the case of copper impurity the higher gradient appears to be more effective in the elimination of the foreign ions, while the lower rate of growth gives better purification as in the case of potassium. Because of the greater dissimilarity of copper and sodium ions, the inclusion of the copper in the crystal is more critically dependent upon growth conditions.

These data indicate that this general method might be applied to the preparation of higher purity raw materials for the growth of single optical crystals. This process is particularly adaptable for this purpose since the same equipment and techniques may be used for the preliminary purification of the material as is used for the growth of the crystal itself. Many substances used for optical crystals are quite difficult

to prepare of sufficient purity by chemical means, notably lithium fluoride[1] and calcium fluoride. This method offers a means of preparing a fairly large amount of purer material in a relatively short time.

ACKNOWLEDGMENT

The writer would like to express his appreciation for the advice and encouragement of Professor D. C. Stockbarger, who suggested the problem.

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Theory of Burning Velocity. II. The Square Root Law for Burning Velocity[1]

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(Received June 27, 1947)

Previous papers by the authors having suggested that the diffusion of active particles (chiefly hydrogen atoms) from the flame front is the controlling factor in combustion in Bunsen-type burners, an equation for burning velocity based on such a concept is derived. This equation shows that the burning velocity should be proportional to the square root of an expression in which the most important factor is the sum of the products $p_i D_i$ for all effective atoms or free radicals, p_i being the concentration of an atom or radical at the flame front, and D_i its coefficient of diffusion into cold, unburnt gas. The burning velocity equation is applied to the combustion of carbon monoxide and hydrogen, and excellent agreement between calculated and experimental values of the burning velocity is obtained. The equation is also used to account for the effect of pressure upon burning velocity.

INTRODUCTION

PREVIOUS papers by the authors on Bunsen-type burner flames (with laminar flow)[3,4] have shown that there exists in moist carbon monoxide flames a close correlation between the calculated equilibrium hydrogen atom concentrations at the flame front and the experimentally determined burning velocity, and have suggested that this correlation can be explained if it is assumed that the diffusion of active particles (chiefly hydrogen atoms) from the flame front into the unburnt gas controls the combustion process. In this paper an equation for burning velocity based on this idea is derived, and is given a number of practical applications.

THE SQUARE ROOT LAW FOR BURNING VELOCITY

As in our Paper I on burning velocity,[4] we consider the simple model of the combustion zone illustrated by Fig. 1. The flame front is defined as the surface where combustion has proceeded to equilibrium, and is used as the origin of a fixed coordinate system. The unburnt gas moves in the direction of the arrow, the flow being taken normal to the flame front, so that in the cold unburnt gas the flow velocity must be the burning velocity as defined in the usual manner. In order to arrive at soluble differential equations, it is necessary to assume that the whole combustion zone is at one constant mean temperature, T_m, which is, in general, taken to be some fraction of the flame temperature, T_1. The effect of this simplification is to give to the density and the flow velocity values ρ_m and u_m, which are constant over the entire combustion zone. It should be pointed out that the actual value chosen for the mean temperature can affect the predicted burning velocity only to a small extent.

We now consider a portion of the flame front of area dS and a cylinder of this same cross-sectional area going from it into the unburnt gas. It is assumed that ignition of unburnt gas can take place at any point in this cylinder by means of active particles (chiefly hydrogen

[1] Abstracted in part from a thesis submitted by Charles Tanford in partial fulfilment of the requirements for the degree of Doctor of Philosophy at Princeton University.
[2] National Research Council Predoctoral Fellow in Chemistry, 1946–47.
[3] C. Tanford and R. N. Pease, J. Chem. Phys. 15, 431 (1947).
[4] C. Tanford, J. Chem. Phys. 15, 433 (1947).

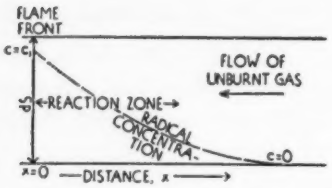

FIG. 1. Model of flame front and combustion zone.

atoms) present there as a result of diffusion from the flame front. The concentration in molecules per cc of any such active particle at any point has already been obtained in Paper I, and is given by

$$c_i = c_{1i} \exp\left(-\frac{B_i u_m}{D_{mi}} x\right) \tag{1}$$

where c_{1i} is the equilibrium concentration of the active particle at the flame front, D_{mi} is the diffusion coefficient of the active particle into unburnt gas at the mean temperature T_m, and B_i is a factor, usually close to unity, which corrects for the loss of radicals due to chemical processes. The evaluation of this last factor for hydrogen atoms is discussed in detail in Paper I.

Now, the rate of formation of combustion product at any point must certainly depend upon this active particle concentration. It can be expected to be the sum of a number of terms, one for each effective atom or free radical. The concentrations of species other than these active particles can also be expected to enter into the expression. For the sake of simplicity we shall assume here that of the latter only the concentration of combustible, C, is of importance, and that the rate of formation of combustion product in molecules per cc per sec. at any point can be represented by

$$d(\text{product})/dt = \sum_i k_i c_i C$$

where k_i is a rate constant appropriate to the ith active species. Then the total rate of formation of product molecules in the cylinder of Fig. 1 in molecules/sec. is

$$\int_{x=0}^{\infty} \sum_i k_i c_i C dS dx.$$

Now, from the initial composition of the combustion mixture it is possible to compute the total rate of formation of combustion product which is required to bring about complete combustion, and this rate must be equated to the above expression. To calculate this rate we consider the volume of gas (measured at 298°K) which crosses the section dS of the flame front per second. This volume is given by the product of the burning velocity (u_0) and the cross-sectional area (dS). If Q is the mole fraction of potential combustion product in this gas,[5] then, where L is the number of molecules in one cc of gas at 298°K, the number of molecules of product required to be formed per second over the cross-sectional area dS for complete combustion must be $LQu_0 dS$. Since, by definition, combustion must be complete at the flame front, we then have

$$LQu_0 dS = \int_{x=0}^{\infty} \sum_i k_i c_i C dS dx.$$

We now substitute for c_i from Eq. 1, and assume a mean value independent of x for the concentration of combustible, so that we obtain

$$LQu_0 dS = \sum_i k_i C c_{1i} dS \int_0^{\infty} \exp\left(-\frac{B_i u_m}{D_{mi}} x\right) dx$$

$$= \sum_i k_i C c_{1i} dS \frac{D_{mi}}{B_i u_m}. \tag{2}$$

The equilibrium composition of the burnt mixture is usually in terms of partial pressures or mole fractions,[5] so that we replace c_{1i} by Lp_i/θ_m where θ_m is T_m/T_0, the ratio of the mean temperature of the combustion zone to the temperature of the unburnt gas (usually 298°K), and L/θ_m therefore the number of molecules in one cc of gas at the mean temperature. Furthermore, the diffusion coefficient varies approximately as the square of the temperature,[6] so that we can replace D_{mi} by $D_i \theta_m^2$, where D_i is the diffusion coefficient of the ith active species into cold,

[5] The compositions of the unburnt gas and of the final equilibrium mixture at the flame front are most conveniently expressed as volumes percent, or, better as mole fractions. We shall use the symbols q_k to represent mole fractions in the unburnt gas, and the symbols p_k to represent calculated equilibrium mole fractions at the flame front. If the flame is at a pressure of one atmosphere, these mole fractions are, of course, equivalent to partial pressures.

[6] S. Chapman and T. G. Cowling, *The Mathematical Theory of Non-Uniform Gases* (Cambridge University Press, 1939), p. 248.

unburnt gas. Finally, the flow velocity, u_m, can be related to the burning velocity, i.e. the flow velocity in cold, unburnt gas, by the relation $u_m = u_0\theta_m$.

Making these substitutions in Eq. 2, we find that L, θ_m, and dS drop out, and we obtain the square root law for burning velocity,

$$u_0 = \left(\sum_i \frac{k_i C p_i D_i}{Q B_i}\right)^{\frac{1}{2}}. \quad (3)$$

Since the existence of combustion limits imposes a relatively narrow range of variability upon the concentration of combustible, C, and upon the mole fraction of potential combustion product, Q, and since the factors B_i vary but little from mixture to mixture, we can say that, for the purpose of comparing the burning velocities of different mixtures in which the same kinetics (i.e., the same k_i) are likely to be involved, the burning velocity must be roughly proportional to $(\sum_i p_i D_i)^{\frac{1}{2}}$. This immediately explains the correlation between burning velocity and hydrogen atom concentration found for mixtures containing carbon monoxide.[3]

APPLICATION TO CARBON MONOXIDE COMBUSTION

In the combustion of carbon monoxide the mole fraction of potential combustion product in the initial mixture is the mole fraction of carbon monoxide, or (since one mole of oxygen can oxidize two moles of carbon monoxide) twice the mole fraction of oxygen, whichever of these is smaller. This is conveniently represented by the symbol $(q_{CO}, 2q_{O_2})<$. If the average mole fraction of carbon monoxide over the combustion zone is, say, 0.7 of that present initially, the average concentration of combustible, C, can be expressed in terms of that initial concentration. For, since the number of molecules in one cc of gas at the temperature T_m is L/θ_m, we then have

$$C = 0.7 L q_{CO}/\theta_m.$$

Considerable evidence exists which suggests that oxygen atoms are not of importance in initiating carbon monoxide combustion (for example, combustion in the absence of moisture, even with an excess of oxygen, proceeds only with the greatest difficulty), so that it appears reasonable to suppose that only hydrogen atoms and hydroxyl radicals of the available active particles are of interest to us. Of these, the contribution of hydroxyl is usually small, because D_{OH} is small. In a few of the mixtures for which calculations have been made, however, the concentration of hydroxyl is very much larger than that of hydrogen atoms, and in those cases good agreement of experimental burning velocities with those predicted by Eq. 3 can be obtained only by inclusion of the part played by hydroxyl. Thus the special form of this equation for carbon monoxide combustion becomes

$$u_0 = \left\{\frac{0.7L}{\theta_m}\frac{q_{CO}}{(q_{CO}\cdot 2q_{O_2})<} \times\left(\frac{k_H p_H D_H}{B_H} + \frac{k_{OH} p_{OH} D_{OH}}{B_{OH}}\right)\right\}^{\frac{1}{2}}. \quad (4)$$

This equation can be simplified to some extent. The correction term B_{OH} is found to be always within one or two percent of unity, and can therefore be neglected. Further, in all mixtures containing chiefly carbon monoxide, oxygen and nitrogen, in any proportion whatsoever, diffusion coefficients have about the same value. At 298°K D_H is 1.95 cm²/sec. (see paper I) and D_{OH} is 0.29 cm²/sec. Finally, we can assume that the rate constant k has about the same value for H as for OH. Placing the mean temperature, T_m, equal to, say, 0.7 of the equilibrium flame temperature, and substituting for L its numerical value, 2.48×10^{19} (298°K, one atmosphere pres-

TABLE I. Burning velocities in carbon monoxide flames.

Composition	$\theta_1 = \frac{T_1}{T_0}$	$P_H \times 10^4$ atmos.	$P_{OH} \times 10^4$ atmos.	B_H	u_0, cm/sec. calc.	obs.[c]
35%CO,[a] 8.5%O₂, 56.5%N₂	5.8	0.1	—	1.08	22	25
26.5%CO,[a] 44.1%O₂, 29.4%N₂	7.8	0.7	20.6	1.23	36	30
40%CO,[b] 12.6%O₂, 47.4%N₂	7.8	2.5	3.4	1.32	37	30
40%CO,[a] 12.6%O₂, 47.4%N₂	7.8	3.8	4.9	1.28	41	40
40%CO,[b] 59.1%O₂, 0.9%N₂	9.1	5.6	56	1.25	51	48
40%CO,[a] 24%O₂, 36%N₂	8.9	11.6	56	1.39	56	51
45%CO,[a] 22%O₂, 33%N₂	9.1	16	58	1.38	59	57
40%CO,[a] 59.1%O₂, 0.9%N₂	9.1	9.2	88	1.25	59	60
60%CO,[b] 39.4%O₂, 0.6%N₂	9.8	24	86	1.35	67	68
50%CO,[a] 30%O₂, 20%N₂	9.4	24	91	1.35	69	72
80%CO,[b] 19.7%O₂, 0.3%N₂	9.6	29	39	1.39	84	72
60%CO,[a] 24%O₂, 16%N₂	9.6	38	90	1.39	81	83
60%CO,[a] 39.4%O₂, 0.6%N₂	9.8	39	134	1.32	81	93
70%CO,[a] 24%O₂, 6%N₂	9.7	52	102	1.37	96	98
80%CO,[a] 19.7%O₂, 0.3%N₂	9.6	59	78	1.37	112	106

[a] CO contains 1.35% H_2O and 1.5% H_2.
[b] CO contains 1.35% H_2O.
[c] G. Jahn, *Der Zündvorgang in Gasgemischen* (Oldenbourg, Berlin, 1934).

TABLE II. Burning velocities in hydrogen flames.

Composition	$\theta_1 = \frac{T_1}{T_0}$	$P_H \times 10^4$ atmos.	$P_{OH} \times 10^4$ atmos.	B_H	u_0, cm/sec. calc.	obs.[a]
40%H_2, 7.5%O_2, 52.5%N_2	5.0	0.1	—	1.02	120	100
60%H_2, 8.4%O_2, 31.6%N_2	5.5	0.6	—	1.04	140	175
40%H_2, 10.5%O_2, 49.5%N_2	6.5	5.6	0.4	1.16	180	200
40%H_2, 15%O_2, 45%N_2	8.3	85	46	1.10	330	300
60%H_2, 12%O_2, 28%N_2	7.3	32	2.5	1.15	320	350
40%H_2, 24%O_2, 36%N_2	9.2	135	380	1.01	390	360
40%H_2, 36%O_2, 24%N_2	9.2	96	520	1.06	390	380
60%H_2, 16%O_2, 24%N_2	8.7	214	50	1.15	530	485
60%H_2, 24%O_2, 16%N_2	9.9	590	400	1.02	700	660
60%H_2, 32%O_2, 8%N_2	10.1	590	890	1.02	690	730

[a] G. Jahn, *Der Zündvorgang in Gasgemischen* (Oldenbourg, Berlin, 1934).

sure), we then obtain

$$u_0 = \left\{ \frac{4.84\times10^{19}k}{\theta_1} \frac{q_{CO}}{(q_{CO}\cdot 2q_{O_2})<} \times\left(\frac{p_H}{B_H}+0.15p_{OH}\right)\right\}^{\frac{1}{2}}. \quad (5)$$

Before this equation is applied, it must be remembered that the burning velocity of carbon monoxide mixtures does not tend to zero as the free radical concentration becomes zero,[7] i.e., there appears to be a small, probably fairly constant contribution to the burning velocity which is not dependent upon the free radical concentration. A plot of burning velocity against the square root of the free radical concentration shows that this radical-independent contribution is about 17 cm/sec. This value agrees closely with burning velocities observed by Ubbelohde and Dommer[8] for carbon monoxide—air mixtures in the complete absence of moisture or hydrogen, i.e., under conditions where H and OH could not be formed. This contribution to the burning velocity must be added to Eq. 5, so that we obtain

$$u_0 = 17+\left\{ \frac{4.84\times10^{19}k}{\theta_1} \frac{q_{CO}}{(q_{CO}\cdot 2q_{O_2})<} \times\left(\frac{p_H}{B_H}+0.15p_{OH}\right)\right\}^{\frac{1}{2}}. \quad (6)$$

Equation 6 has been used to compute burning velocities of a number of mixtures containing carbon monoxide. The constant k is, of course, arbitrary, best fit of the experimental data being obtained with the value 1.64×10^{-13}. Methods for the calculation of the free radical concentrations at the flame front and of the term B_H have been described in previous papers. The results of the calculations are shown in Table I, and it is seen that excellent agreement exists between the calculated burning velocities and experimental values determined by Jahn.[9] It was found that somewhat less good agreement is obtained for extremely rich mixtures (ratio of CO and O_2 greater than 4), and such mixtures have not been included in Table I.

It can be seen at once that the value found for k is of the right order of magnitude. For, converting from the units of cc molecule^{-1} sec.$^{-1}$ to the more familiar units of cc mole^{-1} sec.$^{-1}$ by multiplication by Avogadro's number, we obtain $k=1.00\times10^{11}$ cc mole^{-1} sec.$^{-1}$. This value is entirely reasonable for the high temperatures obtaining in the combustion zone,[10] and suggests that the activation energy of the rate-determining step in the combustion mechanism is about 7 or 8 kcal./mole. The fact that the same value for the rate constant can be used throughout, despite the fact that there is variation in the mean temperature, also requires that the activation be of this order or lower.

APPLICATION TO THE COMBUSTION OF HYDROGEN

Assuming that the mechanism of hydrogen combustion is similar to that of carbon monoxide combustion, we obtain for the burning velocity an equation similar to Eq. 4. Again it is found that there is a contribution independent of the concentration of active particles, this time of about 110 cm/sec., so that the burning velocity equation becomes

$$u_0 = 110+\left\{ \frac{2.48\times10^{19}kD_H}{\theta_1} \frac{q_{H_2}}{(q_{H_2}\cdot 2q_{O_2})<} \times\left(\frac{p_H}{B_H}+0.21p_{OH}\right)\right\}^{\frac{1}{2}}. \quad (7)$$

[7] Reference 3, Fig. 1.
[8] L. Ubbelohde and O. Dommer, J. Gasbel. **57**, 757 (1914).
[9] G. Jahn, *Der Zündvorgang in Gasgemischen* (Oldenbourg, Berlin, 1934).
[10] For reaction at every collision and zero entropy of activation, the bimolecular rate constant is about 10^{14} cc mole^{-1} sec.$^{-1}$.

It should be noted that while the ratio D_{OH}/D_H remains about constant, the value of D_H now depends upon the composition, being 2.35 for mixtures containing 40 percent hydrogen, and 2.6 for mixtures containing 60 percent hydrogen.

Equation 7 has been used to compute the burning velocities of a number of mixtures containing hydrogen, with the best value of k now 6.5×10^{-13} (corresponding to a value of 3.9×10^{11} cc mole^{-1} sec.$^{-1}$), i.e., slightly higher than for carbon monoxide. The computations are shown in Table II, and again good agreement is found between calculated burning velocities and those observed experimentally by Jahn.[9]

THE EFFECT OF PRESSURE ON BURNING VELOCITY

Equation 3 should prove to be very useful in predicting the effect of a number of variables, such as pressure, preheating, nature of diluent gas, etc., upon burning velocity. As an example we shall give here a semi-quantitative estimation of the effect of pressure upon burning velocities in general.

We observe at once that only three of the factors of Eq. 3 depend upon pressure, these being C, p_i, and D_i. Moreover, for a mixture of given initial percentage composition, the concentration of combustible, C, in molecules per cc, is directly proportional to the pressure, while the diffusion coefficients, D_i, are inversely proportional to the pressure. These two effects therefore cancel, and it remains to consider only the pressure-dependence of the free radical mole fractions, p_i. Since these free radicals are products of dissociation, their mole fractions will decrease with increasing pressure, in general roughly as the square root of the pressure. (Slight changes in flame temperature and molecular concentrations always occur, so that an analytical expression is not feasible.) Since the burning velocity itself is proportional to the square root of the p_i, therefore, it should vary inversely, roughly as the fourth root of the pressure. Such an effect has indeed been observed for a number of hydrocarbon flames, as well as for carbon monoxide.[11]

CONCLUSION

It should perhaps be pointed out in conclusion that the very simple treatment of burning velocity given in this paper is successful only because the effects of the motion of the gas stream and of diffusion upon local free radical concentrations are relatively much greater than the effects of chemical processes. In other words, the concentration of active particles at any point depends very little upon the chemical reactions occurring in the gas. Of the latter, we have taken into account only the recombination of hydrogen atoms and the formation of HO_2, and it is very likely that the accuracy of the burning velocity equation could be improved if full consideration could be given to chain branching and other chemical processes which in this simple treatment have been ignored.

[11] L. Ubbelohde and coworkers, J. Gasbel. **59**, 49 (1916), **60**, 225 (1917); L. Khitrin, Tech. Phys. U.S.S.R. **3**, 926 (1936).

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Heat Capacities of Liquids and Vapors

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By the use of an equation previously derived for the energy of vaporization of a liquid: $\Delta E = k(D_l^n - D_g^n)$ (in which k is a constant; $n = 5/3$, and D_l and D_g are the molar densities of liquid and vapor, respectively), an expression is derived relating $(\partial \Delta E/\partial T)_{sat}$ to the difference in molar heat capacities at constant pressure of the liquid and vapor (ΔC_p). At low pressures this relation can be approximated by the equation $\Delta C_p = (\partial \Delta E/\partial T)_s + R$ (R is the gas constant, 1.986 cal./mole-°A). Under these conditions $(\partial \Delta E/\partial T)_s = (5/3)\Delta E(\partial \ln D_l/\partial T)_s$, and the resulting equation for ΔC_p is $\Delta C_p = (5/3)\Delta E(\partial \ln D_l/\partial T)_s + 1.99$. From known properties of liquids ΔC_p can be calculated using this last equation. These calculated values are found to be in good agreement with observed experimental values.

IN a recent paper[1] it was shown that a cage model of a liquid could be used to derive a simple analytic expression for the configurational energy of the liquid. If the same expression is applied to the configurational energy of the vapor in equilibrium with the liquid, the energy of vaporization is given by the difference between these configurational energies:

$$\Delta E_{vap} = E_c(\text{liq.}) - E_c(\text{gas}). \quad (1)$$

Since the configurational energies obtained from the cage model are explicit functions only of the density of the particular phase involved, the energy of vaporization becomes an explicit function of these parameters only, and is given by the following equation:

$$\Delta E_{vap} = k(D_l^n - D_g^n). \quad (2)$$

D_l and D_g are the molar densities of the liquid and gas phases, respectively, k is a constant for any given liquid, and n is a number which may be taken as 5/3 for all liquids.[1] (In the neighborhood of the critical region, the value $n = 2$ gives a better fit with experimental data.)

If we differentiate this expression for the energy of vaporization with respect to temperature at saturation conditions, we will obtain the derivative $(\partial \Delta E/\partial T)_s$,* which may be related thermodynamically to ΔC_p, the difference in the heat capacities of the liquid and its saturated vapor. This latter equation may then be solved explicitly for ΔC_p in terms of experimentally available properties of the liquid and vapor.

[1] S. W. Benson, J. Chem. Phys. **15**, 367 (1947).
* The subscript s will refer to saturation.

RELATION BETWEEN $(\partial \Delta E/\partial T)_s$ AND ΔC_p

From the first and second laws it is possible to derive the following equation for ΔC_p:[2]

$$\Delta C_p = \left(\frac{\partial \Delta E}{\partial T}\right)_s + \left[\frac{\Delta H}{\Delta V} + P\right]\left(\frac{\partial \Delta V}{\partial T}\right)_p + \frac{P\Delta H}{T\Delta V}\left(\frac{\partial \Delta V}{\partial P}\right)_T. \quad (3)$$

Regrouping the terms in Eq. (3) we find:

$$\Delta C_p = \left(\frac{\partial \Delta E}{\partial T}\right)_s + \frac{\Delta H}{T}\left[\left(\frac{\partial \ln \Delta V}{\partial \ln T}\right)_p + \left(\frac{\partial \ln \Delta V}{\partial \ln P}\right)_T\right] + P\left(\frac{\partial \Delta V}{\partial T}\right)_p. \quad (4)$$

Equation 4 is an exact relation between ΔC_p, $(\partial \Delta E/\partial T)_s$, and the known properties of a liquid and its vapor. The first term on the right-hand side of the equation is the dominant term and negative, a fact in agreement with the observed property that the heat capacity of a liquid is greater than the heat capacity of its vapor.

The third term in Eq. 4 is positive, and the second term is made of two partial derivatives, the first of which is positive and the second negative. If equations of state are available, the second and third terms may be explicitly evaluated and ΔC_p calculated exactly. However, at low vapor pressures the vapor is very dilute and

[2] F. H. MacDougall, *Thermodynamics and Chemistry*, (John Wiley & Sons, Inc., New York, 1939) third edition, p. 126, contain a derivation from which Eq. 3 may be constructed.

may be assumed to obey the ideal gas laws. In such regions the following approximations may be made:

$$\left(\frac{\partial \ln \Delta V}{\partial \ln T}\right)_p \sim \left(\frac{\partial \ln V_g}{\partial \ln T}\right)_p \sim 1, \quad (5)$$

$$\left(\frac{\partial \ln \Delta V}{\partial \ln P}\right)_T \sim \left(\frac{\partial \ln V_g}{\partial \ln P}\right)_T \sim -1, \quad (6)$$

and

$$\left(\frac{\partial \Delta V}{\partial T}\right)_p \sim \left(\frac{\partial V_g}{\partial T}\right)_p \sim R/P. \quad (7)$$

Substituting these values into Eq. 4 we have, finally,

$$\Delta C_p \sim \left(\frac{\partial \Delta E}{\partial T}\right)_s + R. \quad (8)$$

EVALUATION OF $(\partial \Delta E/\partial T)_s$

If we take the derivative with respect to temperature of ΔE (at saturation) as given by Eq. 2, we have

$$\left(\frac{\partial \Delta E}{\partial T}\right)_s = knD_l^{n-1}\left(\frac{\partial D_l}{\partial T}\right)_s - knD_g^{n-1}\left(\frac{\partial D_g}{\partial T}\right)_s. \quad (9)$$

Rearranging the terms this becomes

$$\left(\frac{\partial \Delta E}{\partial T}\right)_s = \frac{nkD_l^n}{D_l}\left[\left(\frac{\partial D_l}{\partial T}\right)_s - \left(\frac{D_g}{D_l}\right)^{n-1}\left(\frac{\partial D_g}{\partial T}\right)\right]. \quad (10)$$

At the pressures which are under consideration (in the neighborhood of the boiling point or lower), $(\partial D_g/\partial T)_s$ is never greater than 1/10 of $(\partial D_l/\partial T)_s$. In this same region D_g is usually less than 1/200 of D_l. We can, therefore, make the following approximations in this pressure region:

$$\left(\frac{D_g}{D_l}\right)^{n-1}\left(\frac{\partial D_g}{\partial T}\right)_s \ll \left(\frac{\partial D_l}{\partial T}\right)_s, \quad (11)$$

and

$$\Delta E = kD_l^n. \quad (12)$$

Making the substitutions from Eqs. 11 and 12 into Eq. 10 we find:

$$\left(\frac{\partial \Delta E}{\partial T}\right)_s \sim n\Delta E\left(\frac{\partial \ln D_l}{\partial T}\right)_s. \quad (13)$$

TABLE I. ΔC_p of liquids and their saturated vapors.

Compound	Mole Wt.	t (°C)	ΔC_p(obs.) cal./mole −°C	ΔC_p(calc.) cal./mole −°C
Ethyl ether	74	35	14.0	14.2
Carbon tetrachloride	154	20	11.2	12.1
Benzene	78	80	14.9	14.4
n-hexane	86	80	16.5	15.6
Sulfur dioxide	64	15	11.4	12.7
Water	18	100	9.31	9.21

Further substitution from Eq. 13 into 8 finally yield

$$\Delta C_p = n\Delta E(\partial \ln D_l/\partial T)_s + R. \quad (14)$$

COMPARISON OF EQ. 14 WITH EXPERIMENTAL DATA

Equation 14 gives us a method of calculating ΔC_p at low pressures from the energy of vaporization of a liquid and its coefficient of expansion. If data are lacking for the energy of vaporization, ΔE may be approximated at the boiling point by Trouton's rule or by Hildebrand's rule. In any case, all of the quantities in the first term on the right-hand side of Eq. 14 are either well known or easily measured experimentally. On the other hand, it is very difficult to obtain reliable experimental values for ΔC_p. Heat capacities for liquids have been measured, but heat capacities at constant pressure for saturated vapors are difficult to obtain.

In Table I experimental values of ΔC_p are compared with values calculated with the aid of Eq. 14 ($n = 5/3$).

The experimental values for the heat capacities of liquids and vapors were taken from values listed in Landolt-Bornstein and the *International Critical Tables*. For the calculated values of ΔC_p, Eq. 14 was used, with the value of n taken as 5/3. Values of the energy of vaporization and the thermal coefficient of expansion of the liquid were calculated from the data of Young[3] and tables found in Landolt-Bornstein. The agreement between the observed and experimental values of ΔC_p (Table I) are quite satisfactory and probably within the limits of error of the experimental values for the molar heat capacities. The agreement lends further support to the value of $n = 5/3$ which was proposed in the previous paper.[1]

[3] Young, Proc. Roy. Dublin Soc. 12, 374 (1910).

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The Experimental Determination of the Intensities of Infra-Red Absorption Bands. III. Carbon Dioxide, Methane, and Ethane*

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The absolute intensities of the chief infra-red absorption bands of carbon dioxide, methane, and ethane have been determined experimentally to be (in cycles per centimeter at N.T.P.):

Carbon dioxide	Methane	Ethane
670 cm^{-1} band: 560×10^{10}	1306 cm^{-1} band: 450×10^{10}	820 cm^{-1} band: 73×10^{10}
2350 cm^{-1} band: 8600×10^{10}	3020 cm^{-1} band: 900×10^{10}	1450 cm^{-1} bands: 230×10^{10}
		2950 cm^{-1} bands: 2200×10^{10}

These results are in satisfactory agreement with available data on infra-red dispersion and atomic polarization. They may be interpreted in terms of dipole moments, μ', of bonds between vibrating atoms, and their rates of change with internuclear distance, $\partial\mu'/\partial r$. When this is done for the CH bond, however, unexpected variations in these quantities are found for the different vibrations and molecules studied. The average values are about $\mu'=0.4\times10^{-18}$, $\partial\mu'/\partial r=\pm0.6\times10^{-10}$. For the CO bond the values are considerably larger.

INTRODUCTION

THE light transmitted a distance, L, through a gas at pressure, p, is given by Eq. (1). Here $I_0(\nu)$ is the incident intensity,

$$I(\nu)=I_0(\nu)\exp[-\alpha(\nu)pL], \qquad (1)$$

and $\alpha(\nu)$ is the absorption coefficient. The intensity of absorption is defined by Eq. (2). Here

$$A_i\equiv\int_{i\text{th band}}\alpha(\nu)d\nu, \qquad (2)$$

A_i is the absolute intensity of the ith vibrational absorption band, the integral being taken over the band in question.

Direct measurement of the intensity is difficult because $\alpha(\nu)$ and $I(\nu)$ may fluctuate considerably even over the small frequency range transmitted by an infra-red spectrograph at any setting. A spectrograph with a finite effective slit width averages $I(\nu)$ over that frequency range, and it is not possible to obtain $\alpha(\nu)$ directly from such a measurement. In previous papers an extrapolation procedure has been described for determining A_i from absorption measurements made with a spectrograph of low resolving power,[1] and the application of this method to ethylene and nitrous oxide has been discussed.[2] The results of further measurements using this method will be reported in the following sections. The experimental procedure involves measuring the apparent value of the intensity—called the "integrated apparent absorption coefficient"—as a function of the partial pressure of the absorbing gas, with an inert (non-absorbing) gas added to a constant total pressure. The limit of this "integrated apparent absorption coefficient" as the absorbing gas pressure approaches zero is the true intensity.[1] The inert gas present serves to broaden the individual lines making up the absorption band and reduce the fluctuations in $\alpha(\nu)$ which cause the "integrated apparent absorption coefficient" to deviate from the true intensity.

The absorption of light by these infra-red bands is due to changes in the dipole moment of the vibrating molecule when the atoms are displaced from their equilibrium positions. The intensities are proportional to $|\partial\mathbf{\mu}/\partial Q|^2$, where $\mathbf{\mu}$ is the dipole moment of the molecule, and Q the normal coordinate for the vibrational mode in question.[2] The complete relationship is given in Eq. (3).

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[1] E. Bright Wilson, Jr. and A. J. Wells, J. Chem. Phys. 14, 578 (1946).

[2] A. M. Thorndike, A. J. Wells, and E. Bright Wilson, Jr., J. Chem. Phys. 15, 157 (1947).

$$A_i=(N\pi/3c)\{|\partial\mu_x/\partial Q_i|^2 + |\partial\mu_y/\partial Q_i|^2+|\partial\mu_z/\partial Q_i|^2\}. \quad (3)$$

The intensities may be interpreted in terms of the structure of the molecule by assuming that the dipole moment, $\boldsymbol{\mu}$, of the molecule can be regarded as the sum of dipole moments, $\boldsymbol{\mu}_i'$, of the bonds forming the molecule. With such a picture the intensities of bending modes determine μ', stretching modes $\partial\mu'/\partial r$.[2] These quantities might reasonably be expected to be characteristic properties of any particular bond, constant for different vibrations and different molecules, but the results show that this is true only as a very rough approximation.

In the following sections values are given for the intensities of the fundamental bands of CO_2, CH_4, and C_2H_6. These are interpreted in terms of the properties of CO and CH bonds.

CARBON DIOXIDE

The intensities of the carbon dioxide bands are of special interest because: (a) measurements of infra-red dispersion are available[3] which may be compared with our values for the intensities, and (b) absorption of heat by CO_2 in the atmosphere is important in meteorology. Unfortunately our measurements on CO_2 are less reliable than those on other gases because of the difficulties involved in removing atmospheric CO_2 from the optical path of our spectrograph.

The CO_2 samples were admitted directly to the absorption cell from a Matheson lecture bottle.

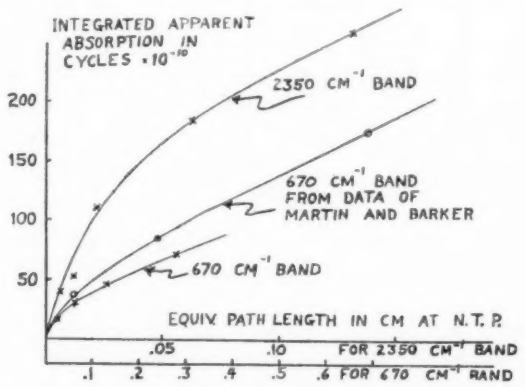

FIG. 1. Experimental data on absorption by carbon dioxide bands at a total pressure of one atmosphere.

[3] These are summarized by O. Fuchs, Zeits. f. Physik 46, 519 (1927).

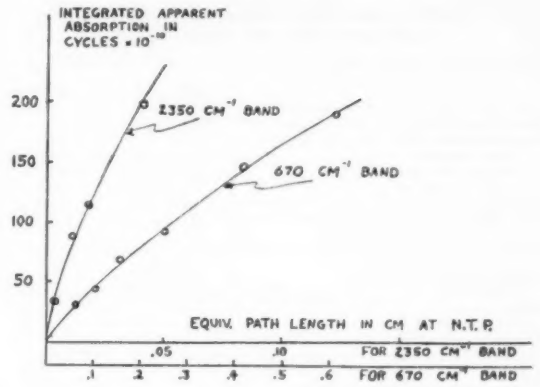

FIG. 2. Experimental data on absorption by carbon dioxide bands at a total pressure of four atmospheres.

The broadening gas was nitrogen obtained from an Air Reduction Company high pressure cylinder. One set of measurements was made at a total pressure of one atmosphere; a second set at about four atmospheres total pressure using a pressure cell. One atmosphere was not enough to give complete pressure broadening, but was probably sufficient to give a fairly close approach to the limiting absorption curve which would have been obtained with complete broadening.

It is obviously necessary to eliminate the absorption by atmospheric CO_2 in the optical path of the spectrograph in order to measure the absorption of the CO_2 sample in the absorption cell even when a blank comparison cell is used. The presence of atmospheric CO_2 introduces an inadmissable frequency dependence of the incident intensity.[1] The atmospheric CO_2 would, in fact, absorb quite completely all frequencies corresponding to the lines in the CO_2 bands, so that addition of CO_2 in the absorption cell would have very little effect upon the transmitted light. The presence of atmospheric CO_2 would, therefore, make the absorption by the CO_2 in the sample cell much smaller than it should be.

In order to remove the CO_2 from the optical path, the spectrograph[2] was enclosed in a housing built of Masonite and plywood.*** The air inside was circulated through Drierite and Caroxite by means of a small blower. At the same time nitrogen was admitted to the housing at a rate of about 10 cubic feet per hour so as to maintain an outward flow through the many small leaks.

*** Dr. Oliver A. Schaeffer assisted in the setting up of this air-conditioning system.

TABLE I. Intensities of carbon dioxide bands (units are cycles per cm at N.T.P.).

	670 cm^{-1}	2350 cm^{-1}
From data of Martin and Barker[a]	660×10^{19}	—
From our data with total pressure:		
1 atmosphere	560×10^{19}	7200×10^{19}
4 atmospheres	470×10^{19}	9600×10^{19}
4 atmospheres	—	8900×10^{19}[b]
Average	560×10^{19}	8600×10^{19}
From dispersion data of Fuchs[c]	538×10^{19}	7680×10^{19}

[a] See reference 4.
[b] A second set of data on the 2350 cm^{-1} band was taken giving this result.
[c] See reference 3.

This procedure, while inconvenient, reduced the CO_2 concentration so that no absorption by atmospheric CO_2 could be observed. In the first set of measurements, however, it was not possible to eliminate the atmospheric absorption completely, and it was necessary to introduce a correction for what remained.

The experimental data are given in Fig. 1 and Fig. 2. In Fig. 1 we also show a curve based on data published by Martin and Barker[4] for the 670 cm^{-1} band. Their resolving power was substantially greater than ours. Since the band at 670 cm^{-1} has a strong Q-branch, "envelope effect" is to be expected,[1] and it is likely that the difference between the two curves is due to the difference in resolving power.

The data given in Fig. 1 and Fig. 2 are values of the "integrated apparent absorption" defined by Eq. (4), where $\mathfrak{B}$ = "integrated apparent absorption,"

$$\mathfrak{B}=\int_{\text{band}}\ln(T_0/T)d\nu, \tag{4}$$

T_0 = light transmitted by blank comparison cell, T = light transmitted by sample cell. The "integrated apparent absorption coefficient," B, defined by Eq. (5)

$$B=\mathfrak{B}/pL \tag{5}$$

was calculated, as before,[2] from points on the smooth curves.

The resulting intensities are given in Table I. The different values are not in particularly good agreement. The experimental errors may, however, be somewhat larger for CO_2 than the 10 percent previously estimated,[2] so that the discrepancies are no larger than should be expected on the basis of experimental errors.

In the case of the 670 cm^{-1} band, difference bands are listed as occurring at 618, 647, 668, 720, and 740 cm^{-1}.[5] We have not, however, tried to correct the observed intensity for contributions from these weak overlapping bands.

The comparison between our values of the intensity and those calculated from Fuchs' expression for the index of refraction is made in Table I. The agreement is satisfactory, considering the larger experimental errors for this substance.

If our intensities are used to calculate the atomic polarization, we obtain 0.68 cc. The value given by Watson and Ramaswamy[6] is 0.81 cc. Again the agreement is about as good as we expect.

The properties of the CO bond moment may readily be calculated from the observed intensities. Since the bending and stretching vibrations have different symmetry, it is only necessary to calculate the effective masses for the two modes. The final values obtained for the bond dipole moment are: $\mu'=\pm1.17\times10^{-18}$, $\partial\mu'/\partial r=\pm6.0\times10^{-10}$. These are similar to the results obtained for N_2O.[2]

This result for μ' may be compared with the conventional values of 2.3×10^{-18} assigned to C=O, and 0.7×10^{-18} assigned to C—O.[7] According to Pauling,[8] resonance in CO_2 involves three structures in about equal proportions:

$$\underset{A}{O=C=O} \qquad \underset{B}{\dot{O}\equiv C-\bar{O}} \qquad \underset{C}{\bar{O}-C\equiv\dot{O}}$$

Since the formal charges cancel out, the observed value of μ' would be the average of that for single, double, and triple bonds. Our low value for μ' implies a small dipole moment of the triple bond. It is evident from the three resonant structures for CO_2 that stretching a CO bond will tend to make it a single bond (which has the greatest length), negative at the oxygen end, so

[4] P. E. Martin and E. F. Barker, Phys. Rev. **41**, 291 (1932).

[5] See, for example, G. Herzberg, *Infrared and Raman Spectra of Polyatomic Molecules* (D. Van Nostrand Company, Inc., New York, 1945), p. 274.

[6] H. E. Watson and K. L. Ramaswamy, Proc. Roy. Soc. (London) **A156**, 144 (1936).

[7] S. Glasstone, *Textbook of Physical Chemistry* (D. Van Nostrand Company, Inc., New York, 1940), p. 542.

[8] L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, Ithaca, 1945), second edition, p. 196.

that $\partial\mu'/\partial r$ should be large, as it is, and negative. Since oxygen in more electronegative than carbon, we should select negative signs for both μ' and $\partial\mu'/\partial r$.

METHANE

In any study of the properties of hydrocarbons methane is a logical starting place. The intensities of the methane bands were not, however, the first to be measured, since it was anticipated that it would be very difficult to secure adequate pressure broadening for methane. The individual rotational lines would be widely spaced because of the molecule's small moment of inertia, and a pressure of one atmosphere would not be expected to provide sufficient pressure broadening. With the pressure cell, however, we were able to employ pressures up to five atmospheres. By using ammonia as a broadening gas considerably more effective pressure broadening was achieved than in the case of non-polar gases. In this way it was possible to make satisfactory measurements of intensities with methane.

The methane was used directly from a Matheson lecture bottle (C.P. grade), without further purification. Ammonia used for pressure broadening was obtained from the Ohio Chemical and Mfg. Company. The experimental data are plotted in Fig. 3. Values of the "integrated apparent absorption coefficient" calculated from these curves lead to the intensities given in Table II.

In Table II a comparison is again made with data based upon measurements of infra-red dispersion. The intensities obtained by the two methods are in good agreement, the differences being well within our experimental error.

As a final check upon these intensities for methane, we may calculate the atomic polarization from them. The result is 0.091 cc, whereas Watson and Ramaswamy[6] obtained 0.08 cc. The agreement is good.

A normal coordinate treatment of methane was made by Rollefson and Havens[9] to determine values of μ' and $\partial\mu'/\partial r$ for the CH bond. Our values are only slightly different, and were obtained by adjusting the values of Rollefson and Havens in proportion to the square root of the

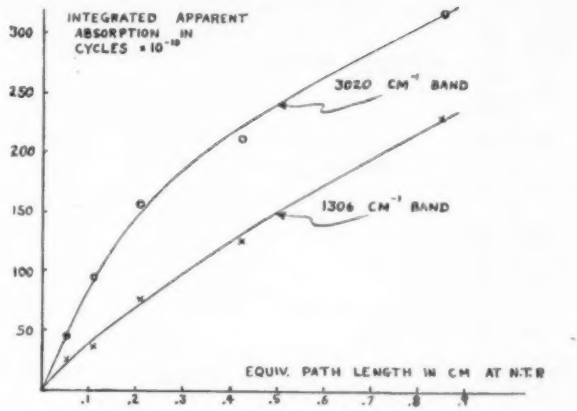

FIG. 3. Experimental data on absorption by methane bands.

intensity. The results are $\mu'=0.31\times10^{-18}$, $\partial\mu'/\partial r=\pm0.55\times10^{-10}$.

These results are in fair agreement with the two values previously reported for the CH bond in ethylene, namely, 0.37×10^{-18} and 0.52×10^{-18} for μ', about $\pm0.6\times10^{-10}$ for $\partial\mu'/\partial r$.[2] As before, the sign of $\partial\mu'/\partial r$ is undetermined. We have followed the usual convention in assuming the bond moment, μ', to be positive at the hydrogen end. Theoretical calculations by Coulson[10] led, however, to a negative value for μ'. Our results do not give any information concerning the sign of μ'.

ETHANE

Measurements were made on ethane following those on methane, since it was desired to compare the behavior of the CH bond in the two related molecules. Ethane was used from a Matheson lecture bottle without subsequent purification. One atmosphere of air was adequate as broadening gas. No attempt was made to reduce atmospheric absorption, which was appreciable only for the bands near 1400 cm^{-1}.

In these experiments it was not possible to

TABLE II. Intensities of methane bands (units are cycles per cm at N.T.P.).

Band	Intensity from these measurements	Intensity from dispersion measurements[a]
1306 cm^{-1}	450×10^{10}	444×10^{10}
3020 cm^{-1}	900×10^{10}	970×10^{10}

[a] See reference 9.

[9] R. Rollefson and R. Havens, Phys. Rev. **57**, 710 (1940).

[10] C. A. Coulson, Trans. Faraday Soc. **38**, 433 (1937).

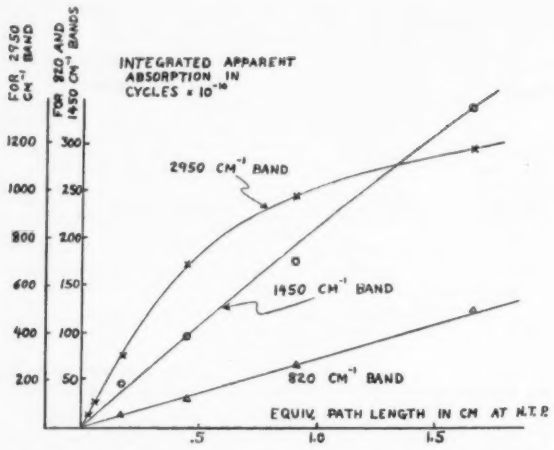

FIG. 4. Experimental data on absorption by ethane bands.

resolve the band at 2954 cm^{-1} from that at 2994 cm^{-1}, nor the band at 1379 cm^{-1} from that at 1486 cm^{-1}. Each of these overlapping pairs of bands is, therefore, considered as a single band in tabulations of experimental data. The frequencies are listed as 2950 cm^{-1} and 1450 cm^{-1}, respectively. The data are presented graphically in Fig. 4. Values of the "integrated apparent absorption coefficient" calculated from these curves lead to the intensities given in Table III.

Unfortunately there are no other data on ethane intensities available which could be used to confirm or deny these results. A very rough check is possible in terms of atomic polarization. Our intensities lead to a calculated atomic polarization of 0.14 cc, whereas the value given by Watson and Ramaswamy[6] is 0.09 cc. This is fairly good agreement, since small atomic polarizations could not be measured very accurately by Watson and Ramaswamy's method.

Values of the intensities of ethylene are also given in Table III. The most striking difference is in the low frequency bending mode which is intense in ethylene but rather weak in ethane. Thus the abnormally great intensity of the out-of-plane bending mode of ethylene[11] has disappeared in ethane. The stretching modes, however, appear to be somewhat more intense for ethane than ethylene.

TABLE III. Intensities of ethane bands (units in cycles per cm at N.T.P.).

Band	Intensity
Ethane:	
820 cm^{-1}	73×10^{10}
1450 cm^{-1}	230×10^{10}
2950 cm^{-1}	2200×10^{10}
Ethylene:[a]	
950 cm^{-1}	1540×10^{10}
1444 cm^{-1}	210×10^{10}
3050 cm^{-1}	840×10^{10}

[a] From reference 2.

A more detailed interpretation of ethane intensities in terms of properties of the CH bond can be made if the intensities of the 1450 cm^{-1} and 2950 cm^{-1} "bands" are broken down into their individual components. Unfortunately, no good basis for estimating the intensities of the individual overlapping bands is available. The best published data appear to be those of Levin and Meyer[12] who, however, failed to resolve either pair completely. Qualitative estimates of the intensities are given by Herzberg.[13]

In the case of the 1379 cm^{-1} and 1486 cm^{-1} bands his estimates are "weak" and "strong," respectively. Levin and Meyer's data indicate fairly clearly that the 1379 cm^{-1} band is a good deal the weaker, and our absorption curves show a weak maximum at about 1375 cm^{-1}. As a rough estimate, therefore, we have assigned 30×10^{10} to the 1379 cm^{-1} band and 200×10^{10} to the 1486 cm^{-1} band.

In the case of the 2954 cm^{-1} and 2994 cm^{-1} bands Herzberg's designations are "strong" and "medium" respectively. The experimental data of Levin and Meyer are consistent with this estimate, but could apparently equally well arise from a weak band at 2954 and a strong one at 2994. In our data the two are completely unresolved. Qualitative consideration of the geometry of the molecule suggests, however, that the band at 2994 cm^{-1} is the stronger, since it is a perpendicular band.[14] On the basis of the

[11] Data on ethylene are discussed in detail in reference 2.

[12] A. Levin and C. F. Meyer, J. Opt. Soc. Am. **16**, 137 (1928). Measurements at higher resolution have been reported (L. G. Smith and W. M. Woodward, Phys. Rev. **61**, 386 (1942)) but no experimental curves given.

[13] See reference 5, p. 344.

[14] The reasoning is as follows: In the ethane molecule the CH bonds are almost perpendicular to the CC bond (the C−C−H angle being about 109°). Therefore a CH bond stretch will give rise to a contribution to μ whose component parallel to the CC bond is small and perpendicular to it is large. In a parallel type band the perpendicular components cancel out, while the parallel components add up to a small net dipole moment. In a perpendicular-type band the parallel components cancel out, while the perpendicular components add up to a large net dipole moment. Therefore the perpendicular type band should be the stronger one.

TABLE IV. Apportionment of ethane intensities.

Band	Frequency in cm^{-1}	Intensity in cycles per cm at N.T.P.	$\partial\mu/\partial Q$
ν_5	2954	200×10^{10}	$\pm$ 45.9
ν_6	1379	30×10^{10}	$\pm$ 17.8
ν_7	2994	2000×10^{10}	$\pm$103
ν_8	1486	$\frac{1}{2}\times\{200\times10^{10}$	$\pm$ 32.5
ν_9	820	73×10^{10}	$\pm$ 19.7

normal coordinate treatment, which will now be discussed, it was determined that the most consistent results were obtained by assigning an intensity of about 200×10^{10} to the 2954 cm^{-1} band and 2000×10^{10} to the 2994 cm^{-1} band. It should be emphasized, however, that these intensities are tentative estimates; only their sum has been accessible to direct measurement.

A simple normal coordinate treatment was carried out for ethane in order to determine the properties of the CH bond moment. It was assumed, following Howard,[15] that the potential function involves only two force constants and may be written as in Eq. (6).

$$2V=K_1\sum_i r_i^2+r_0^2K_2[\sum_i \beta_i^2+\sum_{jk}\alpha_{kj}^2]. \quad (6)$$

Here r_i=change in CH_i bond distance, β_i =change in C—C—H_i angle, and α_{jk}=change in H_j—C—H_k angle. In the latter case the two hydrogens must obviously be attached to the same carbon. $K_1=4.79\times10^5$ dyne/cm, $K_2=0.46\times10^5$ dyne/cm. The method and terminology used follow that of Wilson.[16]

The configuration of the ethane molecule is uncertain to the extent that it may be either "staggered" or "eclipsed." Both lead, however, to the same relations between the observed intensities and properties of bond moments.[17] Our calculations were made on the basis of the eclipsed configuration, but the final results are equally valid for the staggered case.

TABLE V. Characteristics of CH bond moment in ethane (c.g.s. units).

Type of vibration	μ'	μ'/s	$\partial\mu'/\partial r$
ν_6-bending	0.104×10^{-18} or 0.094×10^{-18}	0.096×10^{-10} or 0.086×10^{-10}	—
ν_8-bending	0.35×10^{-18} or 0.33×10^{-18}	0.32×10^{-10} or 0.30×10^{-10}	—
ν_9-bending	0.30×10^{-18} or 0.26×10^{-18}	0.28×10^{-10} or 0.24×10^{-10}	—
ν_5-stretching	—	—	$+0.69\times10^{-10}$ or -0.74×10^{-10}
ν_7-stretching	—	—	$+0.81\times10^{-10}$ or -0.74×10^{-10}

The symmetry coordinates for the infra-red active vibrations were taken to be:

Parallel-type modes

$$\Re_5=(6^{-\frac{1}{2}})(r_1+r_2+r_3-r_4-r_5-r_6),$$
$$\Re_6=(12^{-\frac{1}{2}})[\beta_1+\beta_2+\beta_3-\beta_4-\beta_5-\beta_6 -(\alpha_{23}+\alpha_{13}+\alpha_{12}-\alpha_{56}-\alpha_{46}-\alpha_{45})].$$

Perpendicular-type modes

$$\Re_{7a}=(3^{-\frac{1}{2}})[r_1+r_4-\tfrac{1}{2}(r_2+r_3+r_5+r_6)],$$
$$\Re_{7b}=\tfrac{1}{2}(r_2-r_3+r_5-r_6),$$
$$\Re_{8a}=(3^{-\frac{1}{2}})[\beta_1+\beta_4-\tfrac{1}{2}(\beta_2+\beta_3+\beta_5+\beta_6)],$$
$$\Re_{8b}=\tfrac{1}{2}[\beta_2-\beta_3+\beta_5-\beta_6],$$
$$\Re_{9a}=(3^{-\frac{1}{2}})[\alpha_{23}+\alpha_{56}-\tfrac{1}{2}(\alpha_{13}+\alpha_{12}+\alpha_{46}+\alpha_{45})],$$
$$\Re_{9b}=\tfrac{1}{2}(\alpha_{13}-\alpha_{12}+\alpha_{46}-\alpha_{45}).$$

In terms of these symmetry coordinates the normal coordinates are given by the transformation L^{-1} whose elements are tabulated below:

$$(L^{-1})_{55}=-1.276\times10^{-12}, \quad (L^{-1})_{56}=-0.0177\times10^{-20},$$
$$(L^{-1})_{65}=+0.116\times10^{-12}, \quad (L^{-1})_{66}=-0.903\times10^{-20},$$
$$(L^{-1})_{77}=1.225\times10^{-12}, \quad (L^{-1})_{78}=-0.0040\times10^{-20},$$
$$(L^{-1})_{79}=0.0237\times10^{-20},$$
$$(L^{-1})_{87}=-0.0355\times10^{-12}, \quad (L^{-1})_{88}=0.198\times10^{-20},$$
$$(L^{-1})_{89}=0.808\times10^{-20},$$
$$(L^{-1})_{97}=0.0914\times10^{-12}, \quad (L^{-1})_{98}=-1.313\times10^{-20},$$
$$(L^{-1})_{99}=0.322\times10^{-20}.$$

[15] J. B. Howard, J. Chem. Phys. **5**, 442 (1937).

[16] E. Bright Wilson, Jr., J. Chem. Phys. **9**, 76 (1941).

[17] This may be shown in the following way: We can change from staggered to eclipsed forms by rotating one CH_3 group by 180° about the CC axis. The symmetry coordinates for vibrations parallel to this axis are unchanged, those for vibrations perpendicular to the axis must have coefficients of the internal coordinates belonging to the rotated CH_3 group changed in sign. For example, the symmetry coordinate $\Re_{7a}$ is given by $1/\sqrt{3}[r_1-r_4-\frac{1}{2}(r_2+r_3-r_5-r_6)]$ for the staggered case as contrasted with $1/\sqrt{3}[r_1+r_4-\frac{1}{2}(r_2+r_3+r_5+r_6)]$ for the eclipsed case. In order to set up the secular equation, following the method of reference 16, we calculate the vectors, **S** defined by Eq. (11) of reference 16 as $\mathbf{S}_i^{(i)}=\Sigma_k U_{ik}\mathbf{s}_{ki}$. In the case of $\Re_{7a}$ the **s** vectors are unit vectors along the CH bonds. The U_{ik} are coefficients which give $\Re_{7a}$ in terms of the r's. When one changes from eclipsed to staggered configuration some of the **s** vectors change direction, but the corresponding U_{ik} coefficients change sign so that there is no net change in the **S** vectors or in the secular equation calculated from them. Either form for the molecule will then lead to the same set of L^{-1} coefficients (in terms of symmetry coordinates), and the same values of the $(\partial\mathbf{u}/\partial\Re_k)$'s determined from the observed intensities. The interpretation of the $(\partial\mathbf{u}/\partial\Re_k)$'s in terms of the $(\partial\mathbf{u}/\partial R)$'s, which are properties of individual bonds, again involves the geometry of the molecule and the U_{ik} coefficients, but again in such a way that the changes in these two factors compensate in going from eclipsed to staggered form. Therefore the same results will be obtained for properties of bond moments whichever form of molecule is assumed.

The procedure for calculating the properties of bond dipole moments is the same as that previously described.[2] The perpendicular modes, ν_7, ν_8, and ν_9 are each twofold degenerate, so that only half the observed intensity should be ascribed to each member of these degenerate pairs. The resulting values of intensities and of $(\partial\mu/\partial Q)$'s are given in Table IV, $(\partial\mu/\partial Q)$'s being calculated by Eq. (3).

The values of the $(\partial\mu/\partial Q)$'s and (L^{-1})'s are substituted in Eq. (7) in order to obtain values of the $(\partial\mu/\partial\mathfrak{R})$'s. From these

$$\partial\mathfrak{y}/\partial\mathfrak{R}_k=\sum_i(\partial\mathfrak{y}/\partial Q_i)(L^{-1})_{ik} \qquad (7)$$

latter and the geometry of the molecule the dipole moment, μ', and its rate of change with internuclear distance, $\partial\mu'/\partial r$, may be calculated. If we exclude negative values for the bond dipole moment as unreasonable, the final values are those given in Table V. (Here s is the equilibrium CH distance.) If $\partial\mu'/\partial r$ is positive, the choice of signs for the $(\partial\mu/\partial Q)$'s must be that leading to the top member of each pair of values in Table V. If negative, the bottom member is to be taken.

These results may be compared with those obtained for methane. The outstanding difference between the two molecules is the very low value of μ' obtained for the parallel-type band ν_6 of ethane. The intensity of this band is only about $\frac{1}{10}$ what would be required to give the expected value of μ'. The reason for this is not known and merits further investigation.[18] The values of μ' obtained from ν_8 and ν_9 agree well with that from methane, however, all being close to 0.3×10^{-18}. In the case of $\partial\mu'/\partial r$ the agreement is less satisfactory; values from ethane are about $\pm0.75\times10^{-10}$, whereas $\pm0.55\times10^{-10}$ had been obtained for methane.

These results cast some doubt upon the whole concept of additivity of bond dipole moments. It would seem that the apparent values of μ' and $\partial\mu'/\partial r$ change so much from one molecule to another and one type of vibration to another that strong interactions with neighboring bonds must frequently occur. One might think, however, that our normal coordinate treatment of ethane has been too simple. The potential function with only two force constants does not give very good solutions for the secular equation, and may introduce very considerable approximations in the normal coordinates. Nevertheless the fact remains that the stretching modes are, relatively, too intense in ethane, and the bending modes too weak. The conclusions concerning μ' and $\partial\mu'/\partial r$ are actually not at all sensitive to changes in the normal coordinate treatment.

[18] Such a large discrepancy as this could not be accounted for as an error in dividing the intensity of the "1450 cm^{-1} band" between ν_6 and ν_8. To give ν_6 ten times as much intensity we would have to assign to it all the intensity of the "1450 cm^{-1} band" and more, leaving nothing at all for ν_8.

CONCLUSIONS

Two fairly definite conclusions may be drawn from the results summarized in this and the preceding paper:

(1) Our intensities, obtained by direct measurement of absorption employing an extrapolation to zero absorption, are in satisfactory agreement with results obtained from measurement of infra-red dispersion in all cases where a comparison is possible. Our method may, therefore, be considered reliable and applied with confidence to other molecules.

(2) It is not yet possible to predict intensities of vibrational bands on the basis of empirically-assigned dipole moments for the chemical bonds making up a molecule. If this could be done, it would greatly extend the usefulness of infra-red spectroscopy in the analysis of molecular structure, since the infra-red intensities could be used to determine the numbers of various types of structure present. Further investigations are necessary to measure and explain the behavior of a variety of bond dipole moments under a variety of conditions.

In conclusion the author takes pleasure in acknowledging the continued help of Professor E. Bright Wilson, Jr., under whose guidance these investigations were carried out.

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A Note on the Relation between Entropy and Enthalpy of Solution

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(Received June 2, 1947)

The relation between entropy and enthalpy of solution for a series of non-polar solutes in a given non-polar solvent is discussed. It is considered that solution of a gaseous solute, without changing its concentration on going from gas phase to liquid solution phase, does not change its own entropy, all change of entropy being referred to the solvent. The entropy of the solvent changes because of surface effects around the solute molecules and a kind of long-range order introduced by the solute molecules. Two extreme cases are considered, (1) the case of an ideal solution, and (2) the case of a solute of hard attractionless spheres. The difference in entropy of solution between these extreme cases can be estimated. It can also be estimated by extrapolation from the experimental data on the entropy and enthalpy of solution, and these two estimates agree in order of magnitude. The fact that the relation between entropy and enthalpy of solution is linear is also shown to be a reasonable expectation, and effect of changing solvent as well as solute is considered. The groundwork is thus laid for a qualitative understanding of this relation between entropy and enthalpy of solution.

IT is well known that there is a relation between the entropies and enthalpies of solution of a series of non-polar gases or vapors in a given non-polar liquid solvent, provided the solute molecule is not larger than that of the solvent. This was apparently first remarked by Bell,[1] who noted that some relation between the energy and enthalpy of solution might be expected but gave no explanation of the form of the relation nor of the order of magnitude of the quantities involved; it was further discussed by Barclay and Butler.[2] A rather detailed theoretical discussion has been given by Frank and Evans.[3] In their treatment certain relations used in the discussion of pure liquids[4] were introduced into the theory of solutions only slightly, if at all, modified.[5] It is certainly of interest that this gives an equation which seems to fit pretty well the energy-enthalpy relation for solutions noted above; however, the physical significance and validity of this procedure are not entirely clear. This being the case, it appears that some consideration of this problem from another point of view is still desirable.

In the present note we shall consider the properties of two extreme, hypothetical types of solution, namely (1) an ideal solution, and (2) a solution in which the solute molecules consist of hard spheres, which occupy space but do not exert attractive forces on the solvent molecules. Real solutions may usually be considered to stand somewhere between these extreme types, and it is possible to say something about the transition from one type to the other for any given solvent.

Notation.—Since we shall be interested in entropies of gas and liquid phases for solvent and solute and changes of entropy under various conditions, as well as a number of different volumes and free volumes, we require a system of notation with a variety of subscripts and suffixes, and capital and small letters. In the table which follows, a subscript i is used to denote component i. In the text i takes the value 1 for solvent and 2 for solute. To any of the symbols we may affix an asterisk, indicating that it refers to the case of an ideal solution, or we may add a subscript 0, indicating that it refers to the case in which the solute consists of hard-sphere molecules.

n_i = total number of moles of component i.
N_i = mole fraction of component i in liquid phase.
V = volume of liquid solution containing one mole of solute.
V_i° = molal volume of pure liquid component i.
v_i = molal volume of gaseous component i.
$V_{f,i}$ = molal free volume of component i in liquid solution.
$V_{f,i}^\circ$ = molal free volume of component i in pure liquid phase (see Eq. (5)).

* On leave, 1946–47, from the University of North Carolina, Chapel Hill, North Carolina. This document is based on work performed under Contract No. W-35-058-eng-71 for the Atomic Energy Project at the Clinton Laboratories.

[1] R. P. Bell, Trans. Faraday Soc. **33**, 496 (1937).
[2] I. M. Barclay and J. A. V. Butler, Trans. Faraday Soc. **34**, 1445 (1938).
[3] H. S. Frank and M. W. Evans, J. Chem. Phys. **13**, 507 (1945).
[4] H. S. Frank, J. Chem. Phys. **13**, 493 (1945).
[5] For example, the use of Eq. II(10), together with the subsequent use of β_1 and β_2 as partial molal quantities on p. 508 of Frank and Evans; and the use of Eq. II(21) on p. 513.

S = total entropy of liquid solution.
S_i° = molal entropy of pure liquid component i.
$\bar{S}_i$ = partial molal entropy of component i in liquid solution.
$s_i(v_i)$ = molal entropy of gas at volume indicated.
$\Delta S_i(v_i) = \bar{S}_i - s_i(v_i)$ = entropy of solution of 1 mole of pure vapor component i at molal volume v_i in a large amount of solution of any given concentration (partial entropy of solution).
$\Delta S_i^\circ(v_i) = S_i^\circ - s_i(v_i)$ = molal entropy of condensation of pure component i from molal volume v_i in vapor phase.
ΔS_m = entropy of mixing.
ΔH_i = enthalpy of solution of 1 mole of pure vapor component i in a large amount of any given solution (partial enthalpy of solution).
ΔH_i° = enthalpy of condensation of pure component i.

IDEAL SOLUTIONS

If two liquids form an ideal solution, the entropy of mixing is given by the classical expression

$$\Delta S_m^* = -n_1 R \ln N_1 - n_2 R \ln N_2, \qquad (1)$$

and the total entropy of the solution is given by

$$S^* = n_1 S_1^\circ + n_2 S_2^\circ - n_1 R \ln N_1 - n_2 R \ln N_2. \qquad (2)$$

We then obtain for the partial molal entropy of the solute

$$\bar{S}_2^* = (\partial S^*/\partial n_2)_{T,p,n_1} = S_2^\circ - R \ln N_2. \qquad (3)$$

Let us now consider the entropy of solution of 1 mole of solute from the vapor phase into a very large quantity of solution of any given concentration, with $v_i = V$. This means that the solute enters the solution without change in its volume concentration. We have for this process

$$\begin{aligned}\Delta S_2^*(V) &= \bar{S}_2^* - s_2(V) \\ &= S_2^\circ - s_2(V) - R \ln N_2. \end{aligned} \qquad (4)$$

We can write an equation defining $V_{f,2}^\circ$ as follows:

$$S_2^\circ - s_2(v_2) = R \ln(V_{f,2}^\circ / v_2). \qquad (5)$$

The free volume thus defined includes all effects of communal entropy.

An exactly ideal solution is one in which the solute and solvent are "exactly alike" although distinguishable; that is, their molecules have the same size and force fields.[6] In this case $V_1^\circ = V_2^\circ$ and $V_{f,1}^\circ = V_{f,2}^\circ$. Since V is the volume of solution containing 1 mole of solute, we have $V = V_2^\circ / N_2$. Setting $v_2 = V$, introducing the expression for V into Eq. (5), and substituting in Eq. (4), we obtain

$$\begin{aligned}\Delta S_2^*(V) &= R \ln(V_{f,2}^\circ / V_2^\circ) \\ &= R \ln(V_{f,1}^\circ / V_1^\circ). \end{aligned} \qquad (6)$$

The ratio of molal free volume to molal volume simply represents the effect of neighboring molecules on the space available for the motion of any molecule in the field of those neighbors. Thus the effect of solution without change of concentration is simply the effect of neighboring molecules on the free space available.

NON-IDEAL SOLUTIONS

Equation (6) holds, of course, only for ideal solutions. We may, however, define a new quantity $V_{f,1}'$ by the general equation

$$\Delta S_2(V) = R \ln(V_{f,1}' / V_1^\circ). \qquad (7)$$

$V_{f,1}'$, then, may be said to give that volume left free by 1 mole of solvent for a particular solute. It seems possible, as Frank and Evans have noted, for $V_{f,1}'$ to become as large as, or even greater than, V_1°. At first sight this appears strange, for it seems then that the solute is free to move around in a greater volume than that which contains it, even though this volume itself is well filled with solvent molecules. Frank and Evans pointed out that this could only be explained as an effect of the solute on the solvent. An explanation of the nature of this effect, and an estimate of its order of magnitude, will be the principal aim of the present note.

We now consider the process of solution from a different point of view. We suppose that we have the solute in the volume which it is going to occupy, and pour the solvent in on it. Since this is a liquid system, dilute in the solute, the

[6] There is, of course, no requirement from the thermodynamic definition of an ideal solution (giving the chemical potentials as functions of the mole fractions) that the molecules of solvent and solute be "exactly alike," and there are many solutions, that are very close to ideal, for which this is certainly not the case. However, for a solution to be quantitatively ideal, it seems highly probable that this condition is necessary. It certainly seems to be necessary as far as the size of the molecules is concerned, though this is not very critical. [(See R. H. Fowler and E. A. Guggenheim, *Statistical Thermodynamics* (Cambridge University Press, 1939), pp. 353 ff.)] The effect of the force fields on the ideality of a solution as expressed by Eq. (1) is essentially the subject of the present note. We shall, hereafter, refer to the "exactly ideal" solution described here simply as an ideal solution.

TABLE I. Enthalpies and entropies of solution with acetone as solvent.

	Hard-sphere solute	Ideal solution
Partial enthalpy of solution	$\Delta H_{2,0} = -\Delta H_1^\circ = 7600$	$\Delta H_2^* = \Delta H_1^\circ = -7600$
Partial entropy of solution	$\Delta S_{2,0}(V) = 8$	$\Delta S_2^*(V) = -11.5$
Total entropy of solution	$\Delta S_{2,0}(V) + R = 10$	

Enthalpies in cal. mole^{-1}, entropies in cal. mole^{-1} deg.$^{-1}$

solute molecules may occupy any preassigned positions, regardless of whether the solvent is present or not. We may thus say that the partition function of the solute is unaltered by the presence of the solvent, and we may, somewhat artifically perhaps, refer all entropy effects to the solvent.[7] In considering the entropy of the solvent, we may assume that all solute molecules are held in fixed positions, since in the partition function for the solute all possible positions are included. From this point of view Eq. (7) gives the effect of the solute on the entropy of the solvent; however, a slight correction is required. For it is evident that the process we have just considered gives the total entropy of solution of 1 mole of solute rather than the partial entropy of solution. The total entropy change will be $S - s_2(V) - n_1 s_1^\circ$ instead of $\Delta S_2(V) = \bar{s}_2 - s_2(V)$. Since $S = n_1\bar{s}_1 + n_2\bar{s}_2 = n_1\bar{s}_1 + \bar{s}_2$ (since $n_2 = 1$), we see that the entropy change for the process considered is equal to $\Delta S_2(V) + n_1\bar{s}_1 - n_1 s_1^\circ$. For a dilute solution this may be shown[8] to be equal to $\Delta S_2(V) + R$.

For a solution that is ideal as well as dilute, the total entropy of solution $\Delta S_2^*(V) + R$ of one mole of solute molecules will be negative; this follows from Eq. (6) because $V_{f,1}^\circ$ is always very considerably smaller than V_1°. But in an ideal solution the solvent molecules in the immediate neighborhood of a solute molecule are in the same environment as any other solvent molecules, since the force fields are the same. The lowering of entropy of the solvent implied by Eq. (6) cannot, therefore, be referred to any change in the range of motion of the individual solvent molecules in the neighborhood of solute molecules. It must, on the contrary, be attributed to the introduction of a certain degree of long-range order, produced by having the solute molecules held in fixed position. This restriction in position is transmitted through the neighboring molecules to the solvent, even though the range of motion of these molecules about their equilibrium positions is not altered. It is rather the equilibrium positions themselves which are affected.

To understand better the situation in non-ideal solutions, let us consider the case in which the solute is assumed to be composed of hard-sphere molecules, which exert no force on the solvent molecules. (This means that the enthalpy of solution, $\Delta H_{2,0}$ is actually positive because of the energy necessary to produce the hole in the solvent into which the solute molecule is going to go. Roughly, assuming that the hole is the same size as a solvent molecule, we may say that $\Delta H_{2,0}$ is equal to $-\Delta H_1^\circ$.)[9] If the solute is like a hard sphere, we may expect that a fixed arrangement of solute molecules will be much less effective, if effective at all, in inducing long range order in the liquid. Furthermore, since the energy will not be lowered by proximity of solvent to solute molecules, the solvent molecules around a solute molecule will be reasonably free to arrange themselves in such a way as to allow a maximum of freedom of motion. There will thus be a gain in entropy, similar to the gain in entropy when the free surface of a liquid is increased. This gain in entropy is to be equated to $\Delta S_{2,0}(V) + R$.

APPLICATION TO THE EXPERIMENTAL DATA

Let us now apply these ideas to dilute solutions in a typical solvent, acetone. We use the data collected by Frank and by Frank and Evans,[10]

[7] Somewhat similar considerations have been carried out by R. H. Fowler and E. A. Guggenheim, pp. 372 ff of reference 6, but they did not attempt to consider the solvent effects fully in setting up the chemical potentials. See also Barclay and Butler, reference 2, p. 1454.

[8] We have $\bar{s}_1 = s_1^\circ - R \ln N_1$, since Raoult's law holds for a dilute solution. $N_1 = n_1/(n_1+1)$ with $n_2 = 1$. With $n_1 \gg 1$ this becomes $N_1 \sim 1 - n_1^{-1}$, and $\ln N_1 \sim -n_1^{-1}$, whence the relation follows immediately.

[9] For a calculation of the energy necessary to form a hole in a liquid, see R. H. Fowler, *Statistical Mechanics* (Cambridge University Press, 1936), second edition, p. 844.

[10] H. S. Frank, ref. 4; see especially p. 499; H. S. Frank and M. W. Evans, ref. 3; see pp. 514–515.

and present the relevant material in Table I. The enthalpy values are obtained as indicated from the enthalpy of condensation of acetone. To get $\Delta S_2^*(V)$ we take the entropy of vaporization and the density, and using Eq. (5) (applied, however, to the solvent instead of the solute) calculate that at 25°C the value of $V_{f,1}°/V_1°$ is 0.0030. We then use Eq. (6). The table of Frank and Evans shows how $\Delta S_2(V)$ and ΔH_2 vary from solute to solute. (Actually they list the energy and enthalpy for evaporation from solution to form a gas at 1 atmosphere at 25°C, so their values differ by a sign and a constant additive amount from ours.) By extrapolation we find that the value of $\Delta S_{2,0}(V)$ given in the table is that which corresponds to

$$\Delta H_2 = \Delta H_{2,0} \cong +7600.$$

Had there been no surface effect $\Delta S_{2,0}(V)+R$ would have been zero, assuming that there is no long-range order under these conditions. It is, therefore, natural to compare the $8+R=10$cal. mole^{-1} deg.$^{-1}$ with the surface entropy to be expected. The surface entropy of a liquid is closely related to the Eötvös constant, $-d(V_1°{}^{\frac{2}{3}}\gamma)/dT$, where γ is the surface tension. If we divide this by $N^{\frac{2}{3}}$, where N is Avogadro's number, the expression may be interpreted as the surface entropy per molecule. (This follows because γ is the surface free energy per unit surface, and $(V_1°/N)^{\frac{1}{3}}$ is very close to the surface occupied by a molecule at the surface.) The Eötvös constant for acetone is, from data in the Landolt-Börnstein Tables, 1.8 erg mole$^{-\frac{2}{3}}$ deg.$^{-1}$, which makes $-N^{-\frac{2}{3}}d(V_1°{}^{\frac{2}{3}}\gamma)/dT$ equal to 2.5×10^{-16} erg deg.$^{-1}$. Comparing this to the Boltzmann constant $k=1.37\times10^{-16}$ erg deg.$^{-1}$, we see that the surface entropy is a little less than $2R$ or 4 cal. deg.$^{-1}$ per mole of molecules at the surface.

The surface area about a solute molecule is of the order of four times the area occupied by a molecule at the surface. One would not expect the entropy connected with unit area to be the same as for a flat surface, and the 10 cal. mole^{-1} for the surface entropy in the solution of a hard sphere gas is certainly of the correct order of magnitude.

We may look at this from a slightly different point of view. There will probably be about 10 nearest neighbors about a solute molecule. Each neighbor, therefore, has about 1.0 cal. deg.$^{-1}$ mole^{-1} of surface entropy, about one-fourth as much as a free surface molecule. In a recent paper,[11] we estimated the surface entropy per molecule of a liquid by a rough statistical calculation and found a value about half as great as that given by the Eötvös constant. In our calculation we neglected the decrease in density at the surface layer, which undoubtedly results in an increase in the surface entropy. On the other hand, this decrease in density is probably not appreciable in the neighborhood of a solute molecule. Further, a molecule at the surface of a small spherical hole inside a liquid is not nearly as free as a molecule at a flat surface. Therefore, the value of 1.0 cal. deg.$^{-1}$ mole^{-1} for the solvent molecules about the hard-sphere solute molecule seems entirely reasonable.

We may now be in a position to understand the linear relation between $\Delta S_2(V)$ and ΔH_2, simply as the start of a series expansion. It has, as we have noted, been pointed out by Barclay and Butler that there should be some sort of relation between $\Delta S_2(V)$ and ΔH_2 for a given solvent, and this is also obvious from the discussion given above. We expand about the values for a hard-sphere solute, writing

$$\Delta S_2(V) = \Delta S_{2,0}(V) + a_1(\Delta H_2 - \Delta H_{2,0}) + a_2(\Delta H_2 - \Delta H_{2,0})^2 + \cdots. \quad (8)$$

The question then reduces to a decision as to whether the first term in this expansion is the dominant one. $\Delta S_2(V)$ can be divided into two parts, as discussed above, the surface entropy and the entropy (negative in sign, of course) associated with long-range order, and each one of these can be expanded in a series like Eq. (8).

Let us consider the surface entropy first. As we have noted, this part is contributed by all the nearest neighbors of a solute molecule, and in the range from ideal solution to solution of hard spheres it goes from 0 to 1.0 cal. per mole per deg. for each nearest neighbor, in the case of acetone. This corresponds to a change in the effective free volume of each nearest neighbor molecule by a factor 1.65. Over this great a range the free volume change might be expected to deviate somewhat from being a linear function of the force exerted by the solute molecule on

[11] O. K. Rice, J. Chem. Phys. **15**, 314 (1947).

its neighbors and hence[12] on ΔH_2, and the logarithm of the free volume, which determines $\Delta S_2(V)$, would also be expected to deviate to some extent from being a linear function of the free volume itself. However, these deviations would not be expected to be exceedingly great even with a 65 percent change in free volume, and the experimental data do not actually cover more than about two-thirds of the range between the ideal solution and the hard-sphere solute. And the change in surface entropy contributes only a small part of the variation of $\Delta S_2(V)$ between these extreme types of solution. The greater part of this variation is to be referred to the introduction of long-range order. But this is an effect which is actually shared among many molecules of solvent, so that the change in free volume for any one molecule will be so small that one need have no surprise if the experimental range does not extend beyond that in which the first term of the series expansion of Eq. (8) suffices. This, of course, is not a rigorous explanation of the linearity between ΔH_2 and $\Delta S_2(V)$, but does make it seem plausible. Frank and Evans obtained a linear relation, but this was done by carrying an empirical linear relation between the ΔH's and ΔS's of pure liquids into the equation for the solutions.

The slope of the $\Delta S_2(V)$ *vs.* ΔH_2 line, which may be expressed as

$$a_1=[\Delta S_2^*(V)-\Delta S_{2,0}(V)]/(\Delta H_2^*-\Delta H_{2,0}), \quad (9)$$

is almost the same for a considerable number of solvents. This may be understood in terms of the variation of $\Delta S_2^*(V)$ with ΔH_2^* for a series of different solvents. This, of course, is the same as the variation of $\Delta S_2^\circ(V)$ with ΔH_2°.

Let us write $\delta\Delta S_2^*(V)$ and $\delta\Delta H_2^*$ for the differences between the respective indicated quantities for two solvents. Then since $\Delta H_{2,0} = -\Delta H_2^*$ we will have

$$\delta(\Delta H_2^*-\Delta H_{2,0})=2\delta\Delta H_2^*.$$

This means that if a_1 is to be the same for the two different solvents, we should, from Eq. (9), have

$$\delta[\Delta S_2^*(V)-\Delta S_{2,0}(V)]=2a_1\delta\Delta H_2^*.$$

$\delta\Delta S_{2,0}(V)$ may be expected to be close to zero, because $\Delta S_{2,0}(V)$ is contributed entirely by the surface entropy, and the Eötvös constant has roughly the same value for most common solvents. We might thus expect to find $\delta\Delta S_2^*(V) \cong 2a_1\delta\Delta H_2^*$. Actually, empirically, it is found that $\delta\Delta S_2^*(V)\cong a_1\delta\Delta H_2^*$, since the slope of the $\Delta S_1^\circ(V)$ *vs.* ΔH_1° line for different solvents is approximately the same as that of the $\Delta S_2(V)$ *vs.* ΔH_2 line for solutions with a common solvent. But for the usual solvents $\delta\Delta S_1^\circ(V)$ is such a small fraction of $\Delta S_2^*(V)-\Delta S_{2,0}(V)$ that the empirical relation between $\Delta S_1^\circ(V)$ and ΔH_1° does not require that the $\Delta S_2(V)$ *vs.* ΔH_2 lines for the different solvents be appreciably different. It thus appears that the similar values of a_i for the different solvents may merely reflect the similarity of the solvents used.

On the other hand, the fact that the $\Delta S_1^\circ(V)$ *vs.* ΔH_1° line has about the same slope as most of the $\Delta S_2(V)$ *vs.* ΔH_2 lines for the various solvents is a remarkable fact, noted by Barclay and Butler,[2] but still not fully explained. In going from one solvent to another, for which ΔH_1° is greater, there is no change in surface entropy, since this is zero with either pure solvent or ideal solution; the decrease in entropy arising from long-range order, however, is caused by two factors, (1) the increased force exerted by the particular atom which is condensed into the solution, and (2) the increased force which all neighbor atoms exert on each other. On the other hand, in going from one solute to another which has a greater ΔH_2 in the same solvent there is a decrease in entropy on account of the surface effect, but there is no decrease in entropy on account of factor (2) of the preceding sentence. The surface effect in the case of changing solutes must, therefore, approximately balance factor (2) in the case of changing from one pure solvent to another.

[12] This depends upon the existence of a fairly simple relation between the force exerted by neighbor molecules and the mutual energy, which means that the potential energy curves must in all cases be of similar shape.

Letters to the Editor

THIS section will accept reports of new work, provided these are terse and contain few figures, and expecially few halftone cuts. The Editorial Board will not hold itself responsible for opinions expressed by the correspondents. Contributions to this section should not exceed 600 words in length and must reach the office of the Managing Editor not later than the 15th of the month preceding that of the issue in which the letter is to appear. No proof will be sent to the authors. The usual publication charge ($4.00 per page) will not be made and no reprints will be furnished free.

Halogen-Halogen Distances in Halogen-Polymer Complexes

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October 31, 1947

RECENTLY West has found that many polymers form complexes with iodine, iodine bromide, and bromine.[1] Stretched fibers of these complexes give x-ray spacings characteristic of one-dimensional lattices with periods of 3.10, 2.90, and 2.70A, respectively, characteristic of the halogen but essentially independent of the polymer. West has interpreted the one-dimensional spacings as interatomic distances in linear, polyhalogen chains.

The single, covalent bond distances in I_2, I-Br, and Br_2 are 2.67, 2.47, and 2.28A, respectively,[2] far shorter than the spacings observed by West. If the above spacings are halogen-halogen interatomic distances, their bond numbers are only about 0.17 for all three cases.[3]

While it is easy to visualize a polyhalogen chain with links of bond order $\frac{1}{2}$ (see below), it is hard to understand the virtual elimination of halogen-halogen bonds in the complexes as West's suggestion demands. One possible explanation involves bonding of the halogen atoms to the polymer, but since the polymer fiber spacings are unrelated to that of the halogen separation,[1] this is hardly possible. Moreover, polymer-halogen bonds are undesirable chemically, and will not explain many of the effects observed in the amylose (starch)-iodine complex.[4]

Since, at best, only three orders of the lattice spacing have been observed,[1] it is by no means certain that the halogen atoms in the one-dimensional array are equally spaced. Hence, it is possible that halogen molecules I_2, I-Br, and Br_2 exist in the array, but with somewhat shortened van der Waals separations between molecules.

It has been suggested that a dipole field of a polymer acting on a highly polarizable, linear array of halogen molecules might account for the stability of the halogen-polymer complexes.[4] Recently Mr. R. S. Stein and the author have examined this proposal more quantitatively,[5] and find that very reasonable fields due to the polymer will lead to very materially reduced van der Waals distances between iodine molecules in the iodine complex. A period of 6.2A (twice the observed period) is quite acceptable for an iodine-iodine bonded distance plus a non-bonded van der Waals distance. The proposal also accounts for the very low fugacity of iodine over the complex and the other unusual physical properties of these complexes.

Though polyhalogen chains with equally spaced halogens are allowed by our proposal, they result from resonance of the bond between bonded and non-bonded neighbors as the van der Waals and bonded distances approach each other under the influence of the polymer field. A bond number of $\frac{1}{2}$ would result for each bond, and halogen-halogen distances of 2.85, 2.65 and 2.46A are then expected for the three complexes above. These distances are so far below observed spacings it is unlikely that the limiting case is approached in any known complexes.

Our calculations allow variation in the halogen-halogen distance with dipole field of the polymer. West has noted variations in spacing of 0.15A. This variation is difficult to understand in terms of the polyhalogen suggestion.

In summary, West's observed lattice constants appear too long for polyhalogen chains, but are in excellent agreement with expectations based on the dipole interaction suggestion. Consequently, they tend to substantiate the latter proposal rather than otherwise.

[1] C. D. West, J. Chem. Phys. **15**, 689 (1947).
[2] L. Pauling, *Nature of the Chemical Bond* (Cornell University Press, Ithaca, New York, 1945) second edition, p. 164.
[3] Calculations made in accordance with the rule $R(n)=R(1)-0.3 \log n$, as given by L. Pauling, J. Am. Chem. Soc. **69**, 542 (1947).
[4] Rundle, Foster, and Baldwin, J. Am. Chem. Soc. **66**, 2116 (1944).
[5] R. S. Stein and R. E. Rundle, "The nature of the interaction between starch and iodine" (to be published in J. Chem. Phys.).

Infra-Red Dichroism Involving Hydrogen Bonds

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October 28, 1947

IT is well known that the vibration bands of O−H units which take part in hydrogen bonds are broadened and shifted toward longer wave-lengths. Most spectroscopic investigations of hydrogen bonding have been upon liquids, which can show no orientation effects. This laboratory, in line with its interest in near infra-red dichroism, has in past years made polarized infra-red studies of solid specimens containing oriented hydrogen bonds.[1-3] Such studies are again being undertaken, now with the dicarboxylic acids.

A striking example of dichroism was found in β-succinic acid. Cleavage sections parallel to the crystallographic c axis and approximately 0.2 mm thick were used. The first spectrograms with polarized light, the E-vector vibrating, respectively, parallel and perpendicular to the c axis, were taken in March 1947. No absorption in the 1.4μ unperturbed O−H region (second harmonic) was observed in either run. The run made with the E-vector parallel to the c axis was quite unique; strong absorption started at roughly 1.57μ, increased to opacity at 1.87μ, and remained completely opaque to beyond 2.7μ, the limit of our recording quartz spectrograph.[4] The perpendicular run showed, in contrast, general transparency save for regions of CH_2 overtone and combination band absorption. These latter were of normal intensity for

specimens of the thickness used, the second harmonic CH_2 stretching vibrations, for example, showing about 40 percent absorption.

A similar investigation in the fundamental vibration region for a high temperature modification of succinic acid has recently been reported by D. A. Crooks.[5] He found a great increase in the absorption of the broad band extending from 3250 to 2300 cm^{-1} as the *E*-vector was rotated from the perpendicular to the parallel direction. His conclusion, like ours, is that intermolecular hydrogen bonds are responsible for this broad unidirectional absorption.

The intensity of Crooks' broad hydrogen bond absorption in the fundamental region is, if we interpret correctly, less than $\frac{1}{3}$ that of the fundamental CH_2 valence stretching vibrations at 2900 cm^{-1}. A contrast of these findings with our broad region of complete opacity indicates an anomalous ratio of overtone (and combination) to fundamental mode intensities for the hydrogen bond vibrations.

Data from x-ray diffraction[6] indicate that both the chain axis of the succinic acid molecule and the direction of the intermolecular O—H···O bonds are very nearly parallel to the crystallographic *c* axis. As was remarked by Crooks, the polarized infra-red story bears this out.

X-ray diffraction does not locate definitely the light hydrogen nuclei, their positions on the line connecting the oxygen nuclei of neighboring molecules being the reasonable inference. This inference is strongly supported by the unidirectional nature of the hydrogen bond absorption. It is of interest that no such clear-cut confirmation was found earlier at this laboratory for the looser hydrogen bonds in pentaerythritol.[2]

Adipic acid crystals were also examined with results similar to but not so marked as those of succinic acid. Since the *c* axis of adipic acid crystals, to which the hydrogen bonds are again parallel, is inclined to the surface[7] rather than in it as for succinic acid, conditions are not so favorable.

We have been attempting, up to now with small success, to grow good crystals of anhydrous α- and β-oxalic acid. These, particularly the β-form, should also show the intense hydrogen bonding dichroism. Since there would be no CH_2 absorption in the perpendicular vibration direction, a suitable crystal might be useful as a near infra-red polarizer.

We attempted to make spectrograms of oxalic acid dihydrate specimens but were frustrated by a curious phenomenon. Clear sections became very quickly opaque in the volume through which the converging beam had passed. Presumably water molecules or perhaps ionized portions of these were knocked out of the crystal by the beam in a sort of photo-molecular effect.

A detailed account will be published in the future when observations and the working out of selection rules from the theory of group representations will have been completed. A discussion of CH_2 as well as O—H vibrations will be included.

[1] J. W. Ellis and J. Bath, J. Chem. Phys. **6**, 221 (1938).
[2] J. W. Ellis and J. Bath, J. Chem. Phys. **7**, 862 (1938).
[3] J. W. Ellis and J. Bath, J. Am. Chem. Soc. **62**, 2859 (1940).
[4] J. W. Ellis, Rev. Sci. Inst. **4**, 123 (1933).
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A Spectroscopic Evidence for Activation of Fluorescence by High Valency Manganese Ions

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October 15, 1947

We have measured the emission spectra of manganese activated zinc beryllium silicate and zinc silicate phosphors. The spectrum represented by the number of emitted photons as a function of the frequency was found to be a sum of several gaussian distribution curves, the maxima of each gaussian being at the same frequency for both materials ($h\nu = 2.35$, 2.27, 2.17, and 2.05 electron volts), the relative intensities of the individual components being, however, different. The main band of zinc silicate was found at $h\nu = 2.35$ and that of zinc beryllium silicate at $h\nu = 2.05$ electron volts.

Similarly analyzing the absorption spectra of different manganese compounds in solution, we have found the remarkable fact that the extinction coefficient of K_2MnO_4 in a strong alkaline solution gives rise to the same curves as the emission spectrum of zinc beryllium silicates (see Fig. 1).

The analysis of the absorption spectrum of the aqueous solution of $KMnO_4$ and $Zn/MnO_4/2$ shows the same bands as zinc silicate, but in this case the intensity ratio of the individual bands is different. The position of the bands was found independent of the cation, being determined only by the anion.

These data led us to the conclusion that the emission centers of the fluorescence are associated with the $(MnO_4)^{--}$ and $(MnO_4)^{-}$ ions imbedded in the silicate lattice. This means that in the divalent manganese compound added for activation there is the necessary quantity of the permanganate resp. manganate ions present, or it will be formed during the applied treatment. The number of the negative ions necessary for fluorescence can be estimated

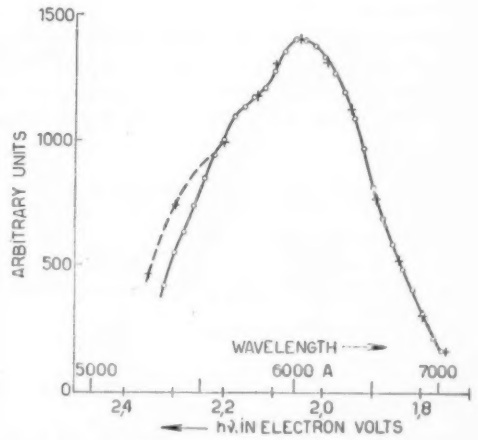

FIG. 1. The ○ denote measured points for the extinction coefficient of K_2MnO_4; the + denote measured points for the emission spectrum of zinc beryllium silicate; ordinate scale for both curves gives the same maximum.

from the saturation value of the emitted fluorescence and by assuming the time of the elementary processes.

For both of these there can be found in the literature only very feeble and uncertain data, but they can still be relied upon for an approximate calculation that the necessary number of centers should lie between 10^{14}–10^{17} centers per gram of fluorescent material.

This means that if the 10^{-4}th part of the present manganese atoms has a valency of six resp. seven, a sufficiently great number of manganate resp. permanganate ions is present to give rise to the measured fluorescence. It is to be noted that the estimated number of these colored anions per unit surface does not cause any perceptible discoloration even in aqueous solutions. Therefore these quantities of the activator anions cannot be detected in the powders by absorption measurements.

Raman Effect of Dichlorohexafluorocyclobutane

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November 13, 1947

LATELY the question of the planarity of the ring in simple cyclic hydrocarbons has been of considerable interest. Recent work[1] indicates that the cyclopentane ring is puckered. On the other hand, Raman and infra-red spectroscopy[2] indicates that the cyclobutane ring is planar while the same seems to be true of the ring in perfluorocyclobutane.[3] This study of dichlorohexafluorocyclobutane was undertaken in connection with this laboratory's interest in this problem.

Dichlorohexafluorocyclobutane is a colorless liquid boiling at 60°C. The material used was furnished by the E. I. DuPont de Nemours and Company. It was further purified by vacuum distillation, dried over $CaCl_2$ for twenty-four hours, and made optically clear by shaking with activated charcoal and filtration through a very fine sintered glass filter. The Raman tube, having a volume of 15 ml, was filled by vacuum distillation.

Exposures were made on Eastman spectrographic plates type 103–0 and type 103a–0, using an Adam Hilger E–2 spectrograph. The Raman tube was suspended in a vertical position with the scattered light being directed into the spectrograph by a right-angle prism. Eight upright mercury arcs arranged in a circle about the Raman tube provided the exciting radiation. Each of these mercury arcs were mounted in front of an individual elliptical reflector which was focused upon the Raman tube. The 4358A line was used as the exciting intensity. Inasmuch as fluorocarbons are notoriously poor light scatterers, exposure times varied from 48 to 172 hours by use of slit widths from 25 to 60 microns. A continuously circulating filter solution of 0.2 percent paranitrotoluene and 0.03 gram of DuPont Rhodamine 5 GDN Extra per liter, dissolved in alcohol, was used[4] to reduce general scattering in the region of 4358A and to eliminate the Raman shifts excited by the 4047A mercury line. The average temperature of the sample was 38°C during the exposures.

TABLE I. Raman lines of dichlorohexafluorocyclobutane.

$\Delta\nu$ cm^{-1}	Estimated relative intensity	$\Delta\nu$ cm^{-1}	Estimated relative intensity
162	S	863	W
216	VW	910	W
270(b)	S	966	S
334(b)	S	1074	W
396(d)	VS	1111	W
465	S	1190	W
490	S	1243	M
561	W	1287	W
640(b)	VS	1392	M
810	VW		

S = strong; M = medium; W = weak; V = very; b = broad; d = diffuse.

We have observed nineteen Raman shifts in dichlorohexafluorocyclobutane. The results are shown in Table I.

We wish to thank Dr. J. D. Park of the Jackson Laboratories of the E. I. DuPont de Nemours and Company for this substance. Further consideration of these results will be published later.

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Phases of Fourier Coefficients Directly from Crystal Diffraction Data

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July 14, 1947

THE intensity of an x-ray beam diffracted from a crystal can be used to find the absolute value of the "crystal-structure factor" $|F_{hkl}|$, but not its phase. However, it appears to be possible to place limits on the phase or, if F_{hkl} is real, to determine the sign, by combining the intensity data from *several* diffracted beams. The general methods for doing this are outlined in the following paragraphs; a detailed article on the subject will appear later.

Although not necessary, it is helpful in strengthening the method to assume that the "atomic-structure factors," f_j, of the atoms in a crystal are related to one another by the relation $f_j = Z_j f$, where Z_j is the atomic number of the j^{th} atom and f is a function of $(\sin\theta)/\lambda$ called "the unitary atomic-structure factor." If there are N atoms in the unit cell of a crystal and

$$Z = \sum_{j=1}^{N} Z_j$$

is the total number of electrons in a unit cell, then

$$\sum_{j=1}^{N} f_j = Zf.$$

Since

$$F_{hkl}=\sum_{j=1}^{N} f_j \exp\left[-2\pi i(hx_j+ky_j+lz_j)\right],$$

the introduction of the f assumption allows one to write

$$\hat{F}_{hkl}=\sum_{j=1}^{N} n_j \exp\left[-2\pi i(hx_j+ky_j+lz_j)\right],$$

where $\hat{F}_{hkl}=(F_{hkl})/(Zf^2)$ and $n_j=Z_j/Z$. $\hat{F}_{hkl}$ is called "the unitary crystal-structure factor" or "the unitary Fourier coefficient." This way of writing assumes that all the atoms in the crystal have the same "shape."

The relation

$$|\sum_{j=1}^{N} a_j b_j|^2 \leqq (\sum_{j=1}^{N} |a_j|^2)\cdot(\sum_{j=1}^{N} |b_j|^2)$$

("Cauchy's inequality") can be applied to the expression for $\hat{F}_{hkl}$. Taking $a_j=(n_j)^{\frac{1}{2}}$ and $b_j=(n_j)^{\frac{1}{2}}\exp\left[-2\pi i(hx_j+ky_j+lz_j)\right]$, one obtains

$$|\hat{F}_{hkl}|^2 \leqq \{\sum_{j=1}^{N} n_j\}\{\sum_{j=1}^{N} n_j|\exp\left[-2\pi i(2hx_j+2ky_j+2lz_j)\right]|\}$$

or $|\hat{F}_{hkl}|^2 \leqq 1$, since

$$\sum_{j=1}^{N} n_j = 1.$$

This result explains the use of the word "unitary" in the name of $\hat{F}_{hkl}$.

If the crystal has symmetry, more interesting relations are obtained from Cauchy's inequality. If, for instance, a center of inversion is present, one can write

$$\hat{F}_{hkl}=2\sum_{j=1}^{N/2} n_j \cos 2\pi(hx_j+ky_j+lz_j)$$

and, noting that $\hat{F}_{hkl}$ is real and applying Cauchy's inequality,

$$\hat{F}^2_{hkl} \leqq 4\{\sum_{j=1}^{N/2} n_j\}\{\sum_{j=1}^{N/2} n_j \cos 2\pi(hx_j+ky_j+lz_j)\}.$$

By the use of $2\cos^2 a=1+\cos 2a$ and elementary rearrangements, it follows that $\hat{F}^2_{hkl} \leqq \frac{1}{2}+\frac{1}{2}\hat{F}_{2h2k2l}$. This important relation requires, for instance, that $\hat{F}_{2h2k2l}$ be positive or zero if $\hat{F}^2_{hkl} \geqq \frac{1}{2}$, or, if $|\hat{F}_{2h2k2l}|>\frac{1}{3}$, then $\hat{F}_{2h2k2l}$ must be positive if $\hat{F}^2_{hkl} \geqq \frac{1}{4}$, etc. Conversely, if this inequality is contradicted, the crystal cannot have a center of symmetry. (This does not invalidate Friedel's Law, which merely states that $|F_{hkl}|=|F_{\bar{h}\bar{k}\bar{l}}|$.)

The presence of other symmetry elements leads to other inequalities which are derived from the appropriate expressions for $\hat{F}_{hkl}$ by using Cauchy's inequality as in the last paragraph. Inequalities for crystals having the several

TABLE I. The inequalities arising from the various axes of symmetry.

Symbol of Axis	Equivalent Symbol	Coordinates	Inequality
1	—	Triclinic	$\lvert\hat{F}_{hkl}\rvert^2 \leqq 1$
$\bar{1}$	—	Triclinic	$\hat{F}^2_{hkl} \leqq \frac{1}{2}+\frac{1}{2}\hat{F}_{2h2k2l}$
2	—	Monoclinic	$\lvert\hat{F}_{hkl}\rvert^2 \leqq \frac{1}{2}+\frac{1}{2}\hat{F}_{2hO2l}$
$\bar{2}$	m	Monoclinic	$\lvert\hat{F}_{hkl}\rvert^2 \leqq \frac{1}{2}+\frac{1}{2}\hat{F}_{O2kO}$
2_1	—	Monoclinic	$\lvert\hat{F}_{hkl}\rvert^2 \leqq \frac{1}{2}+\frac{(-1)^k}{2}\hat{F}_{2hO2l}$
3	—	Hexagonal	$\lvert\hat{F}_{HK\cdot L}\rvert^2 \leqq \frac{1}{3}+\frac{2}{3}\lvert\hat{F}_{H-K\ H+2K\cdot O}\rvert\cos 2\pi\alpha_{H-K\ H+2K\cdot O}$*
3	$3+\bar{1}$	Hexagonal	$\hat{F}^2_{HK\cdot L} \leqq \frac{1}{6}+\frac{1}{6}\hat{F}_{2H2K\cdot 2L}+\frac{1}{3}\hat{F}_{HK\cdot\bar{2}L}+\frac{1}{3}\hat{F}_{H-K\ H+2K\cdot O}$
3_1	—	Hexagonal	$\lvert\hat{F}_{HK\cdot L}\rvert^2 \leqq \frac{1}{3}+\frac{2}{3}\lvert\hat{F}_{H-K\ H+2K\cdot O}\rvert\cos 2\pi\left(\alpha_{H-K\ H+2K\cdot O}+\frac{L}{3}\right)$*
4	—	Tetragonal	$\lvert\hat{F}_{hkl}\rvert^2 \leqq \frac{1}{4}+\frac{1}{4}\hat{F}_{2h2kO}+\frac{1}{2}\hat{F}_{h-k\ h+kO}$
$\bar{4}$	—	Tetragonal	$\lvert\hat{F}_{hkl}\rvert^2 \leqq \frac{1}{4}+\frac{1}{4}\hat{F}_{2h2kO}+\frac{1}{2}\lvert F_{h-k\ h+k2l}\rvert\cos 2\pi\alpha_{h-k\ h+k\ 2l}$*
4_1	—	Tetragonal	$\lvert\hat{F}_{hkl}\rvert^2 \leqq \frac{1}{4}+\frac{(-1)^l}{4}\hat{F}_{2h2kO}+\frac{1}{2}\left(\cos 2\pi\frac{l}{4}\right)\hat{F}_{h-k\ h+kO}$
4_2	—	Tetragonal	$\lvert\hat{F}_{hkl}\rvert^2 \leqq \frac{1}{4}+\frac{1}{4}\hat{F}_{2h2kO}+\frac{(-1)^l}{2}\hat{F}_{h-k\ h+kO}$
6	—	Hexagonal	$\lvert\hat{F}_{HK\cdot L}\rvert^2 \leqq \frac{1}{3}+\frac{1}{3}\hat{F}_{2H2K\cdot O}+\frac{1}{3}\hat{F}_{H-K\ H+2K\cdot O}+\frac{1}{3}\hat{F}_{HK\cdot O}$
$\bar{6}$	$\frac{3}{m}$	Hexagonal	$\lvert\hat{F}_{HK\cdot L}\rvert^2 \leqq \frac{1}{6}+\frac{1}{6}\hat{F}_{OO\cdot 2L}+\frac{1}{3}\lvert\hat{F}_{H-K\ H+2K\cdot O}\rvert\cos 2\pi\alpha_{H-K\ H+2K\cdot O}+\frac{1}{3}\lvert\hat{F}_{H-K\ H+2K\cdot 2L}\rvert\cos 2\pi\alpha_{H-K\ H+2K\cdot 2L}$*
6_1	—	Hexagonal	$\lvert\hat{F}_{HK\cdot L}\rvert^2 \leqq \frac{1}{6}+\frac{(-1)^L}{6}\hat{F}_{2H2K\cdot O}+\frac{1}{3}\cos 2\pi\frac{L}{3}\hat{F}_{H-K\ H+2K\cdot O}+\frac{1}{3}\cos 2\pi\frac{L}{6}\hat{F}_{HK\cdot O}$
6_2	—	Hexagonal	$\lvert\hat{F}_{HK\cdot L}\rvert^2 \leqq \frac{1}{6}+\frac{1}{6}\hat{F}_{2H2K\cdot O}+\frac{1}{3}\cos 2\pi\frac{L}{3}\hat{F}_{H-K\ H+2K\cdot O}+\frac{1}{3}\cos 2\pi\frac{L}{3}\hat{F}_{HK\cdot O}$
6_3	—	Hexagonal	$\lvert\hat{F}_{HK\cdot L}\rvert^2 \leqq \frac{1}{6}+\frac{(-1)^L}{6}\hat{F}_{2H2K\cdot O}+\frac{1}{3}\hat{F}_{H-K\ H+2K\cdot O}+\frac{(-1)^L}{3}\hat{F}_{HK\cdot O}$

* Note: $\hat{F}_{hkl}$ may be expressed $\exp(-2\pi i\alpha_{hkl})|\hat{F}_{hkl}|$. α_{hkl} is the "phase" of $\hat{F}_{hkl}$.

rotation axes, screw axes and rotation-inversion axes are listed in Table I.

It is possible to obtain information on the signs of those $\hat{F}_{hkl}$'s not determined by the inequalities involving only one $|\hat{F}_{hkl}|$[2]. For instance, for the case of a center of inversion, treatment of $|\hat{F}_{hkl} \pm \hat{F}_{h'k'l'}|^2$ by the methods just described yields the relation $|2\hat{F}_{hkl}\hat{F}_{h'k'l'} - \hat{F}_{h+h'k+k'l+l'} - \hat{F}_{h-h'k-k'l-l'}| \leqq 1 + \frac{1}{2}(\hat{F}^2_{2h2k2l} + \hat{F}^2_{2h'2k'2l'}) - \hat{F}^2_{hkl} - \hat{F}^2_{h'k'l'}$. It is probable that further development of this method will provide sign or phase determinations for most of the $\hat{F}_{hkl}$'s of a crystal. That not all of the signs (or phases) can be determined by these methods follows from the ambiguities in crystal structure determination discussed by A. L. Patterson.[1]

It is essential, before using any of these inequalities, that the experimental F_{hkl}'s be expressed in absolute units. In the case of x-ray diffraction, the units are electrons per unit cell.

[1] A. L. Patterson, "Ambiguities in the x-ray analysis of crystal structures," Phys. Rev. **65**, 195 (1944).

Infra-Red Dichroism in Aligned Polythene and "Parowax"

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November 6, 1947

ORIENTED specimens of polythene were examined for dichroism in the 0.6- to 2.7-μ region. These specimens had been very kindly given to us by Dr. Wilfried Heller, now at Wayne University, and his former coworker at the University of Chicago, Hans Oppenheimer. They were plastic films which had been stretched until the alignment of the molecular chain axes was as closely parallel to the stretch direction[1] as possible. The planes of the carbon backbones had a random angular distribution about this direction.

The absorption bands which appeared with unpolarized light were as follows: (1) a weak band at 8237 cm^{-1}; (2) a well defined doublet at 5782 and 5671 cm^{-1}; (3) a very strong doublet at 4322 and 4271 cm^{-1}; (4) a comparatively weak but distinct band at 4216 cm^{-1}; (5), a shallow poorly defined region between roughly 4180 and 4080 cm^{-1}.

The most interesting dichroism was exhibited by the 4216-cm^{-1} band. All the bands were present to some extent for both E-components, vibrating respectively perpendicular and parallel to the stretch direction, but were considerably stronger in the former. The 4216-cm^{-1} band, in contrast, appeared *only* for the E-vector parallel to the stretch direction. Its intensity was considerably stronger than that found with unpolarized light.

Since this band appears distinctly for films as thin as 50μ, it probably involves displacements within the CH_2 groups. It is quite likely an overtone of a fundamental mode in which the change of dipole moment is completely parallel to the chain axis. In their mathematical treatment of an infinite $>CH_2$ chain, Whitcomb, Nielsen, and Thomas[2] derive a fundamental mode in which all the hydrogens vibrate against all the carbons in a direction parallel to the chain axis. They attribute, we believe mistakenly, the 1460-cm^{-1} hydrocarbon band to this mode.

The known strong bands of normal saturated hydrocarbons at approximately 2925, 2853, and 1460 cm^{-1} are usually assigned, on the uncoupled oscillator approximation, to internal vibrations of the $>CH_2$ units. They are considered to be, respectively, the ν_a, ν_s, and δ type modes of a triangular YX_2 molecule. On this same naive approximation, the two pairs of doublets (2) and (3) can be readily assigned to $2\nu_a$, $2\nu_s$, $\nu_a+\delta$, and $\nu_s+\delta$ in that order. In keeping with these assignments, the high frequency component of both doublets was considerably the stronger of the two.

The CH_2 groups lie on planes perpendicular to the chain axis. For uncoupled oscillators it would be expected that harmonics and combinations of ν_a, ν_s, and δ type CH_2 vibrations would be inactive for the E-vector parallel to the chain axis. Although appreciably diminished, both doublets definitely appeared for this E-component. Their intensity was greater than what can be accounted for by imperfect alignment of the polarizer and the fact that we used a converging beam. A reasonable explanation is that for coupled oscillators there is a component of these vibrations perpendicular to the CH_2 planes. It is of interest that in both pairs of doublets the lower frequency (presumably "symmetrical") component showed considerably the lesser diminution for E-vibrations parallel to the stretch direction.

Unpolarized light spectrograms of thin films sliced from a block of "parowax" were essentially identical with those for polythene. The random molecular orientation in the sliced films made useless any polarization study.

Electron diffraction studies of very thin paraffin films, deposited from a drop of ether solution onto a water surface, have shown that the molecular chain axes are oriented normal to the surface.[3] We prepared semi-crystalline films of from 40- to 500-μ thickness by slow cooling of a melt on a hot water surface. To minimize disorientation owing to the heat of the beam, these films were placed at the exit rather than entrance slit of our instrument. Unpolarized light spectrograms gave convincing proof of an excellent alignment of the chain axes normal to the surface. The band at 4216 cm^{-1} was completely missing, and the intensity ratios and general appearance of the observed bands were unmistakably like those of the spectrograms made for polythene when the E-vector was directed perpendicular to the stretch direction.

A detailed account will be published in the future. We intend to investigate the fundamental region with an instrument now under repair. An assignment in agreement with group theory selection rules will be attempted for the bands involving CH_2 vibrations.

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On the Frequency Factor in the Viscosity-Temperature Relationship of Liquids

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November 5, 1947

IN recent publications[1,2] I clarified the term "activation energy" for viscous flow of liquids from the expression

$$\eta = Z \exp\left[\gamma(M/D-d)^{\frac{2}{3}} \cdot N^{\frac{1}{3}}/(\cos 30\,°)^{\frac{1}{3}}/RT\right]. \quad (1)$$

Since it is possible to calculate $E_{\text{vis.}}$ directly according to (1), it is necessary to examine whether it is also possible to calculate the "frequency factor," Z, directly. Eyring *et al.*[3] have derived the equation

$$\eta = (h/\lambda_2\lambda_3\lambda_1) \cdot (F/F_{\ddagger}) \cdot \exp\left[\epsilon_0/kT\right], \quad (2)$$

the symbols being the same as the original ones of Eyring *et al.* The product $\lambda_2\lambda_3\lambda_1$ has been assumed to be approximately the volume inhabited by a single molecule in the liquid state and, hence, it has been put equal to V/N, where V is the molar volume. Eyring *et al.*[4] have further transformed Eq. (2) into

$$\eta = (hN/V) \cdot \exp \Delta E_{\text{vap.}}/2.45RT \quad (3)$$

Now, I find that the non-exponential term representing the "frequency factor" has to be also altered. The modified equation obtained by me is

$$\eta = (hN/V-b) \cdot \exp\left[\gamma(M/D-d)^{\frac{2}{3}} \cdot N^{\frac{1}{3}}/(\cos 30°)^{\frac{1}{3}}/RT\right], \quad (4)$$

introducing a constant b, characteristic of each substance. The symbols in (4) are:—η = viscosity, γ = surface tension, M = theoretical molecular weight, D = density of liquid, d = density of vapor, N = Avogadro number, R = gas constant (in ergs), T = absolute temperature, h = Planck's constant, and V = molar volume. The only unknown factor b in (4) can be easily evaluated by making appropriate substitutions for the experimental values of η, V, γ, D, d, and T, at one temperature. Calculating b from (4) in this manner, Table I shows that b/V_c is nearly the same for all the substances listed for illustration. The ratio of b to V_c, the molar critical volume, is very nearly $\frac{1}{3}$. It follows, therefore, that the factor b introduced in (4) is almost identical with van der Waals' constant b. This observation applies to other non-associated substances also and is valid at temperatures even far above the melting points.

The necessary data have been taken from the International Critical Tables and from Lange's Handbook of Chemistry.[5]

The correction factor b introduced indicates that $\lambda_2\lambda_3\lambda_1$ has to be interpreted as the free volume or a hole in the liquid and not as the total volume inhabited by a molecule. It is quite likely that $hN/(V-b)$ may be a mathematically simplified form of

$$\frac{hN}{V} \cdot \frac{V}{V-b} = \frac{hN}{V} \cdot \frac{(V-b)+b}{V-b} = \frac{hN}{V}\left(1+\frac{b}{V-b}\right).$$

The complete equation would then be

$$\eta = \frac{hN}{V}\left(1+\frac{b}{V-b}\right) \exp\left[\gamma(M/D-d)^{\frac{2}{3}} \cdot N^{\frac{1}{3}}/(\cos 30°)^{\frac{1}{3}}/RT\right]. \quad (5)$$

TABLE I.

Substance	b/V_c
Acetone	0.313
Benzene	0.318
Carbon tetrachloride	0.338
Chloroform	0.338
Cyclohexane	0.346
Ethylene bromide	0.314*
Ethyl ether	0.344
n-Hexane	0.336
Mean.....	0.331

* V_c is calculated as thrice van der Waals' constant.

A somewhat similar idea has been incorporated by Eyring *et al.*[6] in giving an alternative treatment of viscosity by the theory of absolute reaction rates. It is rather premature at this stage to arrive at any definite conclusion regarding the exact significance of the correction factor. However, a mathematical analysis of the factor may be briefly given here. The number of holes n_h per mole of liquid is equal to $V-b/v_h$, where v_h is the increase in volume required to form a single hole.[7] If b/N is the volume of a single molecule, then $v_h = b/N$; since Eyring's interpretation of the "activation energy" as $\Delta E_{\text{vap.}}/n = E_{\text{vis.}}$ is no longer applicable, there seems to be no justification for assuming that v_h is not equal to b/N. Hence,

$$n_h = V-b/b \cdot N.$$

Thus,

$$\left(1+\frac{b}{V-b}\right) = \frac{n_h+N}{n_h}.$$

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[4] See reference 3, p. 493.
[5] N. A. Lange, *Handbook of Chemistry*, (Handbook Publishers, Inc., Ohio, 1944).
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[7] See reference 3, p. 510.

Prism Spectrometry from 24 to 37 Microns

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November 14, 1947

BY the use of a prism of KRS-5 (thallium bromide-iodide) with a refracting angle of 26°, it is possible to make measurements in the infra-red to 37 microns. With a thinner prism it may be possible to extend the observations to 40 microns. The prism was incorporated in a Perkin-Elmer spectrometer. The stray radiation is almost completely removed by the use of reflection filters of LiF and CaF_2. Greater deflections will be obtained by using a filter of NaF beyond 36 microns. The instrument was calibrated by the use of known absorption bands in this region. The dispersion of KRS-5 is very high from 0.546 to 1.00 micron, but from 2 to 15 microns it becomes extremely small. The dispersion is very good from 24 to 37 microns.

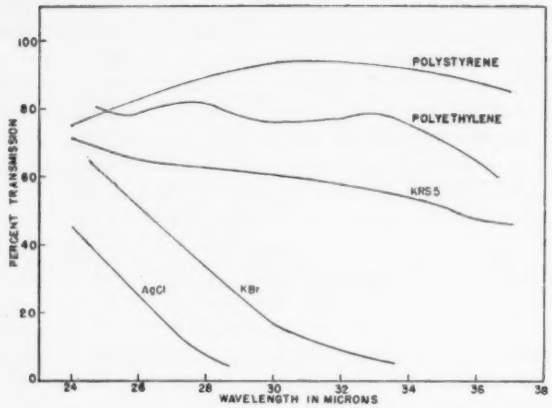

FIG. 1. Transmission of polystyrene 25 microns thick, polyethylene 240 microns, KRS-5 4 mm, KBr 6.4 mm, and AgCl 2.1 mm.

In Fig. 1 is shown the transmission of several materials. The sample of KRS-5 is 4 mm thick and transmits about 70 percent at 24.5 microns. This is about the amount transmitted at 20 microns, and most of the loss is due to reflection. As the wave-length is increased, the transmission decreases, and is 45 percent at 37 microns. Some samples of KRS-5 have less transmission than the sample shown in Fig. 1. One sample examined is opaque beyond 32 microns. This difference between samples obtained from different sources may arise from impurities in the crystals. Polystyrene shows the highest transmission in this region of any substance measured. This is partly caused by the fact that the layer is only 25 microns thick. When a 1-mm thick layer is used only 25 percent of the incident radiation is transmitted at 33 microns. However, for coatings and windows thin films of polystyrene are useful. A layer of polyethylene 240 microns in thickness also shows high transmission in this region. Thinner layers show somewhat higher transmission. The irregular form of the transmission curve is probably caused by absorption bands in the material. Films of C_2F_4, $C_2H_2F_2$, and $C_2H_2Cl_2$ were also measured but they have low transmission in this region. The KBr sample is 6.4 mm thick and transmits about 10 percent at 31.5 microns. Thus, in thicknesses of one mm or less KBr will be useful as a window to 30 microns. A sheet of AgCl, 2.1 mm thick, transmits 10 percent at 27.5 microns. However, the sample is slightly discolored and may not have as high transmission as would be found for a clear specimen. Now that the instrument has been calibrated, investigations are being carried out on a number of liquids and vapors.

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